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PRECONCENTRATION METHODS FOR TRACE ELEMENT DETERMINATION

by

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This research had several objectives. One was to review the literature to determine methods of trace element preconcentration that could be used realistically for sample preparation for trace element determinations in drinking, natural and/or effluent waters. Elements included in the USEPA's listing of Priority Pollutants, with the exception of beryllium, were chosen for the study. Once the methods were identified, those deemed most promising for application to the simultaneous determination of trace elements using energy-dispersive x-ray fluorescence (EDXRF) spectrometry were to be evaluated. Several criteria were used such as the number of elements recovered, linear dynamic range, accuracy and precision, sensitivity-recovery, resistance to interferences and overall ruggedness of the method. Seven methods were eventually selected for detailed evaluation.

Systematic experiments were conducted using bilevel factorial experimental designs for interference studies and single element evaluations of response parameters. The interference studies assessed interferences by concomitant elements, sodium chloride, calcium chloride, and humic organic materials. These choices were made to emulate, as closely as possible, conditions expected to be encountered in natural samples. A numerical rating scheme was devised for the procedures and these values were used to select two optimum methods.

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure chemical pollutants in the environment. As part of this laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Analytical Chemistry Branch develops and assesses new techniques for identifying and measuring chemical constituents of water and soil.

This report presents a factorial study of seven techniques for concentrating trace elements from surface waters. The procedures were evaluated for the 15 Priority Pollutant elements that could be determined by x-ray fluorescence spectrometry. On the basis of objective figures of merit a multielement analytical procedure is recommended that is competitive with atomic absorption spectrometry or with plasma emission spectrometry.

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ABSTRACT

This research had several objectives. One was to review the literature to determine methods of trace element preconcentration which could be used realistically for sample preparation for trace element determinations in drinking, natural and/or effluent waters. Elements included in the U.S. Environmental Protection Agency's listing of Priority Pollutants, with the exception of beryllium, were chosen for the study. Once the methods were identified, those deemed most promising for application to the simultaneous determination of trace elements using energy dispersive x-ray fluorescence (EDXRF) spectrometry were to be evaluated. Several criteria were used such as the number of elements recovered, linear dynamic range, accuracy and precision, sensitivity-recovery, resistance to interferences and overall ruggedness of the method. Seven methods were eventually selected for detailed evaluation.

Systematic experiments were conducted using bilevel factorial experimental designs for interference studies and single element evaluations of response parameters. The interference studies assessed interferences by concomitant elements, sodium chloride, calcium chloride, and humic organic materials. These choices were made to emulate, as closely as possible, conditions expected to be encountered in natural samples.

A numerical rating scheme was devised for the procedures and these values were used to select two optimum methods. The two methods were based on precipitation by either ammonium pyrrolidinedithiocarbamate, or sodium dibenzyldithiocarbamate and performed well in analyses of Certified Reference Materials and comparison studies with atomic absorption and inductively coupled plasma optical emission spectroscopy.

This report was submitted in fulfillment of Cooperative Agreement No. R806520-03 by the University of Denver under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 7, 1979, to May 6, 1982, and work was complete as of August 1, 1982.

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LIST OF ABBREVIATIONS AND SYMBOLS

AC	-- complexation by oxine and adsorption upon activated carbon
APDC	-- precipitation by ammonium pyrrolidinedithiocarbamate
CPG	-- complexation by dithiocarbamate immobilized upon controlled pore glass
DBDTC	-- precipitation by sodium dibenzyldithiocarbamate
NaDDC	-- precipitation by sodium diethyldithiocarbamate
PVP-T	-- precipitation by poly(vinylpyrrolidone) and thionalide
SA-2	-- collection upon ion-exchange resin-impregnated filter paper
AAS	-- atomic absorption spectrometry
AES	-- atomic emission spectrometry
Å	-- Ångström (10^{-10} meter)
CRM	-- certified reference materials
DCP	-- direct current plasma
EDXRF	-- energy dispersive x-ray fluorescence spectrometry
EPA	-- Environmental Protection Agency (U.S.)
ICP	-- inductively coupled plasma
kV	-- kilo (10^3) volts
LiF200	-- lithium fluoride dispersing crystal
m.p.	-- melting point
m/v	-- mass/volume percentage for solutions
nm	-- nanometer (10^{-9} m)
ppb	-- parts per billion (micrograms/liter, $\mu g \cdot L^{-1}$)
ppm	-- parts per million (milligrams/liter, $mg \cdot L^{-1}$)
PTFE	-- poly(tetrafluoroethylene)
Si(Li)	-- lithium drifted silicon semiconductor wafer
UV	-- ultraviolet (radiation)
WDXRF	-- wavelength dispersive x-ray fluorescence spectrometry
μA	-- micro(10^{-6}) amperes

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SECTION 1

INTRODUCTION

As the amount and diversity of the anthropogenic input to the environment changes, so too does the demand upon analytical techniques to monitor environmental changes. This is particularly so in the case of trace metals in the natural and processed water systems where the balance between biological toxicity and dietary necessity is narrow and frequently ill-defined. It is, therefore, becoming necessary to determine a wide range of elements at ever lower concentrations in an increasingly wide variety of samples. In addition, improved accuracy and precision are constantly being sought. In recent years, the use of atomic absorption spectrometry (AAS) (1) with either conventional flame or electrothermal atomization has enabled the widespread, routine determination of many elements, especially metals, in the low mgL^{-1} (ppm) and μgL^{-1} (ppb) concentration ranges. However, with the requirement for identifying and measuring a large number of elements in a single sample, the difficulty of implementing multielement determinations by AAS is becoming an increasing limitation of that method. The more recent and highly successful introduction of atomic emission spectrometry (AES) using high temperature inductively coupled plasma (ICP) sources shows most of the benefits of AAS with the additional advantage of simultaneous multielement determination capability (2). This latter advantage may be brought about either in a truly simultaneous mode through the use of detector arrays or by the use of rapid scan sequential elemental determination. Using either of these approaches, it is possible to determine as many as 40 elements over very wide linear working ranges down to the μgL^{-1} concentration level. Despite these advances, multielement determination in natural and effluent water samples in the low μgL^{-1} (ppb) range is not performed without problems. Many of the difficulties arise from the complex matrices frequently encountered in environmental samples.

The multielement capability of AES is a significant advantage which is shared by comparatively few other analytical techniques. Energy dispersive x-ray spectrometry (EDXRF) is one such technique applicable to all elements with atomic number greater than eleven. Unfortunately, EDXRF has insufficient sensitivity for the determination of trace amounts of the elements. If this technique is to be used for the determination of trace elements in water, then a preconcentration step is mandatory. This may not be a significant disadvantage to EDXRF, as by its very nature preconcentration may yield a sample less subject to potential matrix interferences. It is methods of preconcentration for energy dispersive x-ray spectrometry which are addressed in this report.

tube operated at 30 kV and 0.30 mA in a pulsed mode using a 0.025 mm thickness Ag foil filter. Spectra were collected for 200 s real time.

MULTIELEMENT CALIBRATION

A series of 20 multielement standards was prepared and used for calibration purposes. The elemental concentrations ranged from 0 to 200 µg/100 mL and were prepared in a variety of concentration:ratio values. These are symbolized below in the format "C(n)" where "C" is the concentration of the element (µg/100 mL), and "n" shows the number of standards containing the concentration "C".

Fe(III): 0(6), 5(2), 10(3), 20(4), 50(2), 100(2), and 200(1)
Zn(II): 0(6), 2(2), 5(3), 10(2), 20(4), 50(2), and 100(1)
Pb(II) Tl(I) Hg(II) Se(IV) Cu(II)
Ni(II) Co(II) Mn(II) Cr(VI) As(III): 0(6), 0.5(2), 1(2), 2(2), 5(2), 10(2), 20(2), and 50(2)

One of the 20 standards was a reagent blank and two others contained all the elements at various levels. Calibrations were performed on k-ratio vs. concentration after peak deconvolution by "Super ML," a vendor-supplied program. The k-ratio is the term used by the vendor to indicate the ratio of the sample peak intensity in a selected energy range to that of a pure single element reference spectrum over the same energy range.

MULTIELEMENT STUDY DATA HANDLING PROCEDURES

Energy-dispersive x-ray spectra were collected from 4-14 keV over 1024 channels and stored (on floppy disk) before analysis. "Super ML," a program using digital filtering for background suppression before a multiple least squares peak fitting routine based on reference spectra was used throughout for deconvolution of the complex spectra obtained. The reference spectra were collected from dithiocarbamate precipitates of 100 µg of the pure element of interest under identical conditions to the sample spectra. The K_α, K_β lines of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, and Se and the L_α, L_β lines of Hg, Tl and Pb were used--all these element lines being analyzed simultaneously and deconvoluted. The ratio of the unknown (standard) fitted peak to the reference peak (k-ratio) and the elemental standard data (12 elements 20 standards) were entered into an extended version of "Regal" (a linear regression fitting program) to yield elemental calibration data. After the initial calibration for each element/method, the whole data acquisition and processing cycle was performed in a fully automatic mode.

SAMPLES AND SAMPLING

The natural water samples were collected in Colorado at the points indicated in Appendix A. Samples were collected by surface sampling and were immediately filtered through a 0.45 µm membrane filter on site. After filtration, samples were acidified to pH < 2 using 50% nitric acid ("Ultrex").

Many published methods are available for the preconcentration of environmentally important elements (3-4). Of these, seven were selected for extensive evaluation and comparison. These seven were selected as they had been previously reported to perform well in the analysis of natural water samples, and were capable of forming homogeneous thin film samples well-suited to x-ray analysis. This latter benefit meant that such samples would not suffer from matrix or interelement absorption/enhancement effects yielding much simpler spectral analysis and quantification. The methods chosen for evaluation used several different chemical approaches.

Many of the methods reported offer serious obvious drawbacks which eliminated them from further consideration. For example, in some cases the degree of manipulation, risking contamination, is too great. In other cases, the total chemical capacity is too small and the selectivity insufficient to permit trace level (μg/L) determination of some elements in the presence of minor (mg/L) concentration of other elements; especially important in industrial waste water analyses. Other methods were rejected because of unavailability of reagents or difficulty in their preparation. Methods which provided available reagents, ease and simplicity of use, adequate chemical capacity, and some previously reported success in water analysis were candidates.

(a) AC: Complexation by 8-hydroxyquinoline(oxine) and adsorption of the complexes on activated carbon (5-6)

Complexation of ions in solution by 8-hydroxyquinoline (oxine) and the subsequent adsorption of the complexes onto the surface of activated carbon particles provides a means of preconcentration of the ions from solution. This particular method was chosen as one of the preconcentration procedures for detailed evaluation because of the potential ability of the technique to recover ions from solution which were complexed by organic materials present in the solution. For example, many environmental waters will contain trace or minor concentrations of organic materials such as humic and fulvic acids. These compounds result from the decomposition of previously living organic material. They generally contain sites such as carboxylic acids, phenols, and other oxygenated functional groups capable of reacting to form salts or complexes with metallic ions. The basic concept of the AC technique is to adsorb neutral metal complexes of oxine onto the activated carbon surface. It is reasonable to assume that similar complexes formed with the naturally occurring humic and fulvic acids will be adsorbed. The major disadvantage of this technique is that highly pure activated carbon is not routinely available. An extensive and time-consuming purification technique is required. However, an amount of highly purified activated carbon adequate for several hundred determinations may be prepared in one lot. The most difficult problem associated with this technique is the physical manipulation of the activated carbon during filtration and sample preparation. Other problems which became apparent were that a rather accurate estimate of the total ion concentration in the solution was required for reagent adjustment purposes, and a

rather lengthy equilibration time to quantitatively adsorb the complexes on the activated carbon were required.

(b) APDC: Precipitation by Ammonium Pyrrolidinedithiocarbamate (7)

The use of ammonium pyrrolidinedithiocarbamate (APDC) as a preconcentration reagent is very well established. This reagent has been used for solvent extraction for preconcentration and separation techniques for determination of trace elements using atomic absorption spectrometry. However, the fact that x-ray spectrometry is better suited for determinations using solid samples, solvent extraction applications of this or other reagents was not considered practical, nor does it have any particular advantage. Dithiocarbamate reagents are among the widest spectrum complexing agents available; a wide variety of metal ions form complexes with this functional group. Therefore, application of dithiocarbamates to solvent extraction and/or precipitation is deemed highly desirable. X-ray spectrometry provides more than adequate spectroscopic selectivity to permit the determination of many elements present in a single sample. Therefore, selective precipitation reagents are, in fact, not desirable in this case. The goal is to recover quantitatively as many ions as possible from the solution at the lowest possible concentration. The dithiocarbamate functionality offers further advantages. APDC had been well demonstrated (7) to form precipitates viable as x-ray spectrometric samples. The reagent is commercially available in high purity forms, and procedures for its use as a precipitating reagent are well established. Therefore this method was a prime candidate for the detailed evaluation.

(c) CPG: Complexation by a dithiocarbamate previously immobilized on controlled pore glass (8-9)

As described above the dithiocarbamate functional group is a broad spectrum complexing reagent for metal ions. The resulting complexes may either be extracted into an organic solvent, or allowed to precipitate or co-precipitate from an aqueous solution. An alternative is to immobilize the dithiocarbamate on a suitable substrate and, by passing the solution over this substrate, allow the metal ions to be extracted to its surface. Previous work in our laboratory had demonstrated the potential for the use of controlled pore glass particles as a substrate for the immobilization of dithiocarbamate functional groups (8-9). By packing the resulting material into a column, and passing the sample solution through the column, preconcentration factors as large as 10^4 could be readily achieved. This means that trace elements from as much as one liter of solution may be recovered on as little as 100 mg of modified controlled pore glass. The material could then be removed, prepared in some sample form suited for x-ray spectrometry, and multielement determinations performed. Although the reagent is not commercially available, the preparation was deemed sufficiently simple to make this technique a candidate for evaluation.

There are two major difficulties encountered with the technique. One is a general disadvantage of immobilized or bound functional groups; it is difficult to obtain adequate chemical capacity. Typical capacities are on the order of approximately 1 to 3 milli-equivalents per gram of controlled pore glass. Although this is competitive with commercial ion exchange resin materials, it is not adequate to permit the determination of low ppb levels of an element in the presence of and therefore in competition with high ppm levels of other elements. The second disadvantage is the required manipulation of the particles to prepare the sample. The controlled pore glass (approximately 50 micron particle diameter) must be removed from the small preconcentration column, dried, and placed into some suitable sample form. This is a tedious procedure and creates a distinct disadvantage.

(d) DBDTC: Precipitation by sodium dibenzyldithiocarbamate (10)

The advantages of the dithiocarbamate functional group for precipitation reagents have been given above. The reagent sodium dibenzyldithiocarbamate is not readily commercially available. However, it was demonstrated in the literature to offer some advantages over other available dithiocarbamate reagents. An important advantage is more metal ions present at trace levels are quantitatively recovered by precipitation using sodium dibenzyldi-thiocarbamate than with commercially available dithiocarbamate reagents. As described in this report, the preparation of the reagent in a high purity form in sufficient quantity for several hundred determinations requires at most a few hours of laboratory work. The reagent is stable and may be stored for an indefinite period in the dark under refrigeration. As will be shown in the conclusions in this report, selection of this reagent was an extremely important decision.

(e) NaDDC: Precipitation by sodium diethyldithiocarbamate (11)

Sodium diethyldithiocarbamate is also a well-established, commercially available reagent for the extraction and/or precipi-tation of trace metal ions. This reagent is a simple aliphatic amine-based dithiocarbamate and is, therefore, more stable than the aromatic derivatives. However, being a low molecular weight compound, the metal complexes formed with the reagent tend to be more water soluble than the aromatic derivatives. However, the fact that this reagent is readily commercially available in high purity form and has been repeatedly described in the literature as a reagent suitable for the precipitation of trace elements from water, it seemed only reasonable that the reagent should be a candidate for the detailed evaluation. Other advantages and disadvantages are similar to those described above for the other dithiocarbamates reagents.

(f) PVP-T: Precipitation by thionalide using poly(vinylpyrrolidone) as a carrier (12)

Precipitation by thionalide using poly(vinylpyrrolidone) as a carrier is a technique which was developed under support of the Environmental Protection Agency by researchers at the Naval Research Laboratories, Washington, D.C. The application of the technique was published during the course of this project (12). Because it was a method specifically designed for the EPA, and developed by a major research laboratory, it was considered worthwhile to investigate in more detail. Although thionalide is commercially available in a pure form, acquisition of the recommended poly(vinylpyrrolidone) proved to be a difficult task. The latter reagent was available in small quantities only upon a special request for a research sample. The selection of the method as a candidate for detailed evaluation proved to be questionable. As will be seen in the report, this method provided minimal capability for trace element determination in water samples. Few elements were recovered to any degree, and the filtration of the resulting precipitate was so difficult as to prove the 25-mm-diameter filters totally useless. In order to obtain filtration rates such that 100 ml samples could be filtered in less than one hour, 47-mm-diameter filters were required. It was shown by experimentation and calculation that this rate of filtration was consistent in both diameter filters. The filtration time was proportional to surface area of the filter. Using 47-mm-diameter filters, filtration could be obtained in approximately 15 to 20 minutes. Reducing the filter diameter to 25 mm reduced the filter surface area by a factor of 3.5 and increased the filtration time proportional to that factor to almost one hour.

(g) SA-2: Filtration through a cation exchange resin-impregnated filter paper (13-14)

The temptation to use simple ion exchange materials for the recovery of trace ions from solution is great. Several reports of the use of ion exchange resin-impregnated filter papers had been made in the literature (13-14). On the surface this appears to be an extremely simple and attractive technique for trace element preconcentration. In principle, passing the sample through such a filter paper would be adequate for the recovery of the trace ions in the solution. These ion exchange resin-impregnated filter papers are commercially available. However as received, they are usually highly contaminated with metal ions particularly Fe and other transition elements. Therefore, an extensive cleaning procedure is required. Furthermore, it is necessary to condition the dry resin in the filter paper prior to its use. As the resin-impregnated filter paper may be envisioned as a very short ion exchange column, the efficiency of that column is poor. As a result, several filtrations are required to quantitatively remove the trace ions from solution. Two other major disadvantages exist. As mentioned above, it is difficult to obtain sufficient chemical capacity using a form of immobilized reagent such as an ionic exchange resin. The total capacity of a 25-mm-diameter ion

exchange resin-impregnated filter is only a few hundred micro-equivalents. The ion exchange functionalities which are commercially available on these resin-impregnated papers are not adequately selective to permit the determination of elements such as those on the Priority Pollutants List without the recovery of less significant elements such as calcium, sodium, etc. As a result of the low capacity and selectivity, the resin-impregnated tends to load with ions of little interest. Nonetheless, the commercial availability of the resin-impregnated filter papers and the speed of the procedure mandated the evaluation of this technique as a sample preconcentration procedure for x-ray spectrometry.

The objective of this project was to evaluate these methods in their published forms and on the basis of the criteria outlined below:

(a) Ability to form a homogeneous thin film sample

(b) Number of elements on the EPA Priority Pollutants (15) list (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Hg, Tl, Pb) which are recoverable and detectable by x-ray spectrometry.

(c) Extent of calibration range

(d) Linearity of calibration

(e) Overall method precision

(f) Applicability to natural water samples

(g) Resistance to concomitant element and matrix interferences

(h) General analytical utility, ruggedness and availability of reagents and materials

From the results of the critical comparison of the methods with regard to the above criteria, a procedure is proposed for the ranking of the methods considered.

As essential as the response characteristics of the available methods are, the possibilities of interference are of equal overall importance. Two major categories of interference were considered, chemical and spectral. Spectral interferences arise from partial or total x-ray emission peak overlap. The possibilities for these spectral interferences are many, but are easily predicted with knowledge of the analyte, matrix and analysis conditions, and are frequently simple to correct.

Chemical interferences upon the preconcentration methods are usually more difficult to predict and to correct. Two major categories may be identified for chemical interferences, organic and inorganic. Organic interferences often arise from the presence of humic materials in natural waters (16). Such materials are considered to be high molecular weight polymers containing aromatic rings highly substituted with both phenolic and

carboxylic functional groups (17-18), and have been shown to form complexes with a number of environmentally important metal ions (19-20). Inorganic interference may arise through the presence of concomitant trace elements in the sample, or from major or minor concentrations of salts such as sodium chloride and calcium carbonate in saline or treated industrial effluent waters respectively. All of the above possible interferences were considered for the methods studied.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The evaluation and comparison phases of this research resulted in a rather strong conclusion that the most effective methods of preconcentration were those based upon the addition of precipitation reagents containing the dithiocarbamate group. Several qualitative justifications may be given. These reagents are very broad in the scope of ions with which they will react. The use of various immobilized reagents, or surface adsorption is limited in chemical capacity. Even materials of very high specific surface area must be added in gram quantities to provide millimolar capacity. Although the trace elements to be determined are present in μgL^{-1} concentrations levels, none of the reagents or materials tested were sufficiently selective to be free from reaction with ions of higher concentration. Thus, in a direct consideration of chemical capacity, added soluble reagents which react to form highly insoluble precipitates have the advantage. On the basis of reagent sensitivity to organic materials, the precipitating reagents also hold the advantage. Immobilized reagents may be made ineffective because of blockage of the surface sites by the adsorption of humic and similar materials. These qualitative concepts are supported by the results of the more objective numerical rating scheme which was developed during the course of the research. Furthermore, fully subjective evaluation supported the procedures associated with precipitation and filtration rather than those of immobilized reagents and/or adsorption of complexes. To document these comments, specific observations will be given for each type of preconcentration method evaluated.

The methods employing dithiocarbamate functional groups bound to control pore glass (CPG) as well as the strong acid ion exchange resin impregnated into filter paper (SA-2) have some common disadvantages. Although the CPG offers better selectivity for heavy metals and is less subject to interferences from Ca^{2+} and NaCl, both the CPG and SA-2 methods suffer from limited chemical capacity. This means that in the presence of ions of relatively high concentration, the chemical sites may become saturated and thereby reduce recovery. The SA-2 procedure is convenient and the materials are commercially available. The CPG method is tedious in sample handling after enrichment and the materials are not available commercially.

The use of oxine as a complexing agent for subsequent adsorption of the neutral metal complexes onto activated carbon has many potential advantages. The reagent is well understood, the chemistry of oxinates is well documented, and oxine (8-hydroxyquinoline) is readily available in high purity. In addition, the proposed recovery of metals bound to humic and fulvic compounds

are recovered by the adsorption of these components onto the activated carbon as well. Yet, there are several short falls in the method. One of the most important is that the amount of oxine added to the sample depends too severely for routine use upon the composition of the sample. Large (ppm) concentrations of alkaline earth ions ($Ca^{2}+$, $Mg^{2}+$, etc.) form precipitates with oxine, thus competing with reaction with trace pollutant metal ions. This can be partly compensated if the concentration of these ions is known in advance or can be estimated to within several percent. In a routine application, this would generally not be practical. A second important concern is that the highly purified activated carbon required to serve as the adsorption substrate is not available commercially. This could be overcome, but the purification procedure is lengthy and tedious. Finally, the handling, specimen preparation, and x-ray scattering from the carbon make it less than ideal as a substrate. One thought that occurred to us repeatedly during the work was to use low temperature ashing of the carbon after adsorption, followed by dissolution of the residue. Such a procedure may be useful for preconcentration for atomic absorption or emission spectrometry. Although the oxine/activated carbon procedure fared reasonably well in the evaluation, in real samples with highly varied composition, especially with respect to hardness, this method presents serious drawbacks.

The method of preconcentration using poly(vinylpyrrolidone) and thionailide (PVP-T) performed very poorly. The number of ions quantitatively recovered was very small and did not include some of the more important cases. For example, because atomic absorption is not particularly sensitive for the determination of the As, Se, and Sb, x-ray methods would be useful. However, the PVP-T method failed to perform well in such examples. Furthermore, it was difficult to filter. The original research leading to the published method employed a 47-mm-diameter filter. Using such a filter, 10 to 15 minutes filtration time was required. For our spectrometer a maximum filter diameter of 25 mm is acceptable, which is much more common today than a 47-mm sample diameter. It was shown that using a 25-mm diameter filter, the filtration time increased to well over one hour and was very close to the inverse ratio of the filter area. Therefore, for several reasons the PVP-T method is rated low subjectively as well as by the rating method.

The precipitation of trace elements using one of the reagents sodium diethyldithiocarbamate, ammonium pyrrolidinedithiocarbamate, or sodium dibenzyldithiocarbamate is an effective preconcentration method. The chemistry of the dithiocarbamate functional group provides high selectivity for transition and heavy metal ions. As a result, the presence of alkali and alkaline earth elements in the sample has minimal effects. These reagents, especially the dibenzyldithiocarbamate, form highly insoluble complexes which precipitate metallic ions from solutions as low as a few PPB in concentration. These precipitates form excellent durable specimens for x-ray spectrometric analysis when collected on membrane filters. Few special precautions are required. Common sense precautions are to be sure that sufficient reagent is employed for the sample and that the pH adjustment is carefully performed. An important precaution is to avoid precipitation of an excessive amount of material. When thin, low-mass precipitates are collected, x-ray matrix effects are nil. However, if larger masses are collected, this may not be the case. A more fundamental problem with the

collection of larger masses is the potential losses because the material does not adhere as well to the filter. With proper care, none of these precautions create undue difficulties.

The results of the studies proved that precipitation of trace ions with the sodium salt of dibenzyldithiocarbamate with subsequent filtration on a membrane filter and analysis of that filter with energy dispersive x-ray spectrometry (EDXRF) can provide reliable, simultaneous determinations of as many as fifteen (15) elements from the Environmental Protection Agency Priority Pollutants list (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Hg, Tl. Pb). Concentrations as low as 2-5 μgL^{-1} may be determined in a 100 mL sample with an accuracy and precision of approximately 5-10%. Analysis time and cost are reasonable and certainly competitive with AAS and ICP. The conclusions fall short of supporting the recommendation of preconcentration/EDXRF as a replacement method for AAS or ICP. However, they do strongly suggest the method as an alternative. The success of the use of UV-irradiation to reduce the concentration of organic interferants provides a simple method for the elimination of the problem. In most cases of natural water analyses, the preconcentration/EDXRF method was less subject to interferences and matrix problems than AAS. This is most obvious in cases of large variations in the concentration of minor elements in the sample.

The results clearly suggest that preconcentration/EDXRF should serve as a reliable and economical method for trace element determinations in natural, drinking and effluent waters. The technique should definitely be considered for multielement screening analyses such as industrial effluent waters. It is probable that the development of a detailed procedure would be required for each case. However, this is true with other spectroscopic techniques as well. One cannot expect good results from atomic emission techniques without matrix matching or other precautions specific to the problem. The simplicity of sample preparation, the durability and longevity of the prepared specimens, and the economy of the use of energy dispersive x-ray spectrometry for simultaneous multielement determinations are significant advantages. It is recommended that the Environmental Protection Agency support such analytical methods for the rapid and reasonably accurate screening of industrial effluent and environmental waters. Such a capability could protect against serious spike pollution resulting from failure of industrial water treatment processes.

The cases in which the preconcentration/EDXRF method fail to provide total elemental concentration in the sample are often related to some type of speciation such as oxidation state of the ion. These limitations can be turned into an advantage. This report illustrates several examples such as the determination of the concentration of oxidation states of Cr, As and Se in water samples.

SECTION 3

MATERIALS AND APPARATUS

REAGENTS AND SOLUTIONS

Standard aqueous solutions (1000 mg L^{-1} as the metal) were prepared, whenever possible, by dissolution of the pure metal or oxide in nitric acid with the exceptions of $NiCl_2 \cdot 6H_2O$, $AgNO_3$, $Pb(NO_3)_2$, and $Mn(NO_3)_2 \cdot 6H_2O$ ("Gold Label," Aldrich Chemical Co., Milwaukee, WI 53233). Final acid concentrations were 1% v/v and acids of the highest purity were used throughout (Ultrex, J. T. Baker, Phillipsburg, NJ 08865). Carbon filtered and double deionized water was used for dilution. Solutions and samples were stored in acid-washed (50% HNO_3, 1 week then deionized water, 1 week) linear polyethylene containers.

Poly(vinylpyrrolidone) was obtained as a dry powder (type NP-K90, GAF Corp., 140 W. 51st Street, New York, NY 10020) of average MW = 360,000. Activated carbon (Merck, Rahway, NJ) was purified according to a previously published method (21). Controlled pore glass 200-400 mesh (CPG-10, Electro-Nucleonics, Fairfield, NJ) having a nominal particle diameter of 75 Å, pore volume of 4.0 ml g^{-1} and a surface area of 110 m^2 g^{-1} was used as substrate for the immobilization of N-β- aminoethyl-γ-aminopropyltrimethoxysilane (Z6020, Dow-Corning, Midland, MI 48640) as described previously (10,22). The resulting surface bound amine yielded an exchange medium with a capacity of 0.5 mmol $Cu \cdot g^{-1}$. Subsequent reaction of the bonded amine with CS_2 yielded the bis-dithiocarbamate functionality. Membrane filters 25 mm dia., 0.45 μm pore size (GA-6, Gelman Sciences Inc., 600 S. Wagner Road, Ann Arbor, MI 48106) were used to collect precipitates. Strong acid cation exchange resin-impregnated filter papers (SA-2, Reeve-Angel, 9 Bridewell Pl., Clifton, NJ) were prewashed with three 40 mL aliquots of saturated brine followed by 5 mL deionized water. This procedure ensured presence of the resin in the Na^+ form and removed the majority of the Cu and Fe contamination generally found in the filters. Humic and fulvic acids were prepared from Irish peat by extraction and were purified by dialysis. Sodium dibenzyldithiocarbamate is not currently available commercially and was synthesized in the following manner (34):

> Dissolve 38.5 mL dibenzylamine in 50 mL acetone and cool below 0°C. Add slowly, with constant stirring, a solution of 12 mL CS_2 in acetone (13 mL) keeping the temperature below 5°C. Dissolve 4.4 g NaOH in 20 mL deionized water and cool below 5°C. Add this latter solution maintaining the temperature below 5°C. At this point the solution becomes dark reddish brown. Keeping the temperature as low as

practicable, evaporate 30-40 mL acetone from the liquor. Add 50 mL diethyl ether and evaporate 40-50 mL of the liquid. Repeat the ether evaporation step three times when crystals will appear and then a further four times. Filter the crystals under vacuum and wash several times with cold diethyl ether to yield a snow-white product (m.p. 241-242°C). This method is similar to that of Linder (7) but uses a much lower temperature to yield a high quality product with a higher melting point.

APPARATUS

Wavelength dispersive x-ray spectra were collected using a Philips Model PW-1410 spectrometer. The choices of Mo or W anode x-ray tube, tube voltage and filament current was optimized for each element. A LiF 200 analyzing crystal in conjunction with a proportional gas flow (operated at 1.6 kV) and/or scintillation detector was used. Counting times were usually 100 secs but never exceeded 200 s and instrument control was under the control of an Apple II (Apple Computer Inc., Cupertino, CA) microcomputer (23).

Energy dispersive x-ray analyses were performed using a Spectrace 440 spectrometer (Tracor X-ray, Mountain View, CA) equipped with a Si(Li) detector and interfaced to a TN2000 analyzer (Tracor Northern, 2551 W. Beltline Highway, Middelton, WI 53562) under the control of an LSI 11 microcomputer (Digital Equipment Corp., Maynard, MA). A silver anode 50 watt side window x-ray tube (Kevex Corporation, Palo Alto, CA) was operated in a pulsed mode at an anode voltage of 30 kV for all elements except Hg (40 kV) and at an anode current (usually 300 μA) ensuring a dead time of ≤50% through the whole system. For the AC and CPG methods 200 μA anode current was used. A 0.025 mm thickness Ag foil filter was used to reduce spectral background. All samples, with the exception of those produced by the controlled pore glass method and blanks (1000 s) were irradiated for 200 secs real time with dead times being automatically compensated for.

Thin film samples were mounted between Mylar films (0.000025 in. thickness, Chemplex Ind. Inc., 140 Marbledale Road, Eastchester, NY 10707) in a polypropylene sample holder (Type 1430, Chemplex Ind. Inc.).

The atomic absorption spectrometer was a Perkin Elmer Model 2380 (Perkin Elmer Corp., Norwalk, CT) equipped with a three slot burner or a HGA 2000 carbon furnace atomizer controlled by a HGA 400 programmer and hollow cathode lamps supplied by the instrument vendor. The inductively coupled plasma optical emission spectrometer (Model QA 137, ARL, Sunland, CA) used an all-argon plasma and a direct reading polychromator. The d.c. plasma optical emission spectrometer (Spectraspan III, Spectrametrics, Andover, MA) was operated with an argon plasma and a direct reading polychromator.

Ultraviolet irradiation of samples was accomplished at 254 nm using six 130-mL quartz tubes positioned radially 3 cm from a 550 W medium pressure mercury vapor arc lamp (Hanovia, Ace Glass, Vineland, NJ).

SECTION 4

EXPERIMENTAL PROCEDURES

PRECONCENTRATION PROCEDURES

Sodium Diethyldithiocarbamate (NaDDC)

Samples (100 mL) were adjusted to pH 4 ± 0.05 and buffered with 2 mL 0.1 M potassium hydrogen phthalate solution (pH = 4). Five milliliters 0.1% m/v aqueous solution of NaDDC (Baker) were added with stirring. After aging the precipitate for 15 minutes the solution was filtered under vacuum through a 25 mm 0.45 μm pore size membrane filter and the filter air-dried and mounted between Mylar films.

Ammonium Pyrrolidinedithiocarbamate (APDC)

The APDC procedure was as for the NaDDC method with the exceptions that 1 mL 1% m/v aqueous APDC solution was added and the precipitates were aged for 20 minutes before filtration.

Sodium Dibenzyldithiocarbamate (DBDTC)

The DBDTC procedure was as for the NaDDC method with the exceptions that 1 mL 1% m/v methanolic DBDTC solution was used and precipitates were aged for a total of 30 minutes.

Complexation with 8-hydroxyquinoline ("Oxine") and Adsorption of Complexes on Activated Carbon (AC)

Samples (100 mL) were adjusted to pH 8 ± 0.1 with ammonium hydroxide and buffered with NH_4Cl/NH_4OH solution (10 mL, pH = 8). An amount of oxine solution (8 $mg \cdot mL^{-1}$ in acetone) as determined from the recommendations of Van Grieken (8-9), was added followed by 100 mg activated carbon. The resulting suspension was then rotated in a glass vessel on a pot mill for 1 hour after which time the activated carbon was collected by filtration of the solution through a membrane filter. The filter with the collected activated carbon was mounted between Mylar films while still moist. The lower Mylar support was perforated and the sample dried under vacuum.

Dithiocarbamate Immobilized on Controlled Pore Glass (CPG)

Two hundred milligrams of the derivatized glass beads were loaded into a PTFE column (50 mm length, 4 mm i.d.) and supported at each end by

polypropylene frits. Samples (100 mL) adjusted to pH 8 and buffered with NH_4Cl/NH_4OH (pH = 8) solution were forced down the column under nitrogen pressure (filtration rate: 30-40 $mL \cdot min^{-1}$, N_2 pressure: 25 p.s.i.). The glass beads were then removed from the column, dried in a vacuum desiccator, homogenized and mounted between Mylar films.

Ion-Exchange Resin-Impregnated Filter Papers (SA-2)

Samples (100 mL) were adjusted to pH 3.00 ± 0.05 with 0.1 M phosphoric acid and 2 mL of 3.0×10^{-3} M phosphate buffer added, then filtered seven times through the same 25 mm ion exchange filter paper at a flow rate of 40 ± 10 mL min^{-1}. The air-dried filters were then mounted between Mylar films.

Precipitation with Thionalide and Poly(vinylpyrrolidone) (PVP-T)

Five milliliters each of a 0.1% aqueous solution of PVP-T and a 0.1% m/v solution of thionalide (mercaptoacetic acid--napthylamide) in glacial acetic acid were added to a 100 mL sample. The pH of the solution was adjusted to 4.00 ± 0.05 with 4.0 M ammonium hydroxide and the solution filtered through a membrane filter (47 mm dia., 0.45 µm pore size) after 15 minutes stirring and 5 minutes aging. Twenty-five-mm-diameter sections of these filters were then punched out, air-dried, and mounted between Mylar films for x-ray analysis.

CALIBRATION CURVES FOR RESPONSE STUDY

Single element calibrations were established over the range 0 to 100 µg. Twenty-one standards were used for each calibration curve, five of which were reagent blanks, five of 1 µg, five of 30 µg and duplicates at each of 20, 50, and 100 µg of the element. From these data one detection limit as defined by Currie (24), the precision at 30 µg (300 ppb), the calibration slope, linearity and linear range were established.

PROCEDURE FOR INTERFERENCE ASSESSMENT

The preconcentration methods for each of the 15 elements were assessed at an analyte concentration of 200 µg L^{-1} (ppb). A five-fold excess (1 ppm) of the interferents Cr, Mn, Fe, Co, Cu, Zn, Pb, and Cd was used with sodium chloride (salinity) at 0.5% m/v and Ca at a level of 100 ppm (as Ca^{2+}). The study was operated using a two-level factorial design using complete confounding of second and higher order effects (25-26). The error estimate of this procedure was derived indirectly by running an experimental unit with 16 separate measurements for only 10 potential interferents. The five additional degrees of freedom were carried along without assigning them a specific effect. The results from these "dummy" parameter determinations were taken as an error estimate (27).

Energy dispersive x-ray spectrometry was used for all elements except Ag and Cd (where WDXRF was used through necessity). A silver anode x-ray

Such samples were analysed within 48 hours where possible but are expected to remain stable for a minimum of 6 months. Sample storage was in prewashed (1 week 50% nitric acid, 1 week deionized water) linear polyethylene bottles.

Several secondary standards supplied and certified by various sources were utilized to check the accuracy and precision of the overall analytical method. These standards and their respective sources are listed in Appendix B.

REDUCTION CONDITIONS

This procedure was used for the determination of As(V) after reduction to As(III). To a 100-mL sample 3-mL concentrated HCl (Ultrex) and 1 mL KI solution (4 g/100 mL) were added and the solution brought to boil. Aliquots of 1 mL ascorbic acid solution (2 g/100 mL) and 0.25 mL sodium thiosulfate solution (0.2 g/100 mL) were added at 15-minute intervals and after 45 minutes boiling the solution was cooled to room temperature. The pH of the resulting solution was adjusted to 4.00 ± 0.03 using ammonium hydroxide and the As(III) was precipitated by DBDTC. These conditions are essentially those published by Moore (34). For further studies, the KI and ascorbic acid solution concentrations were increased to 8 and 4 g/100 mL, respectively. This modification tended to lead to better As recovery, particularly when the heating time was increased from 45 to 60 minutes.

SECTION 5

RESULTS AND DISCUSSION

RESPONSE CHARACTERISTICS

At the outset of a large comparison study such as this, several requirements must be identified in order to develop meaningful evaluation experiments. In this study, we have confined our interest to elements of environmental importance and concern as defined in the EPA list of Priority Pollutants (15). Beryllium is the exception and is not included here as routine x-ray spectrometry is unable to detect elements of such low atomic number. As we are concerned with levels of elements commonly found in natural waters, the methods for preconcentration should have a linear dynamic range extending from the low (~10) $\mu g\ L^{-1}$ (ppb) region into the low $mg\ L^{-1}$ (ppm) region. The inherent specificity of the x-ray spectrometric technique means that selective preconcentration methods are largely unnecessary and even undesirable unless used to determine selected species. Thus, the method of choice should be capable of the quantitative recovery of the Priority Pollutant elements in the presence of the "macro" (Group Ia and IIa) elements at environmental levels. In addition to the chemical requirements the method of choice would be one which is simple, inexpensive and insensitive to operator and laboratory variations. In order to evaluate the response characteristics, three analytical criteria were chosen for study:

1. Linear range
2. Sensitivity
3. Reproducibility

The linear range of all the preconcentration methods is governed, at the lower limit, by the ability of the x-ray analytical instrumentation to detect the element of interest. In turn, the lower limit of detection (LLD) is influenced by the background in the spectral region of interest. This spectral background in both the energy and wavelength dispersive instruments arises from many sources but is principally due to scatter of the exciting radiation by the sample. This scatter becomes particularly severe as the average atomic number of the matrix decreases and may be expected to be particularly evident in the predominantly organic matrices used in this study. A lower limit of detection based upon the standard deviation of the blank determination has been used throughout. In addition to the lower limit determined by the x-ray measurement process, the recovery of the elements of interest must be consistent at low ppb levels to permit presentation of the analyte to the instrument. The upper limit of the range is also governed by both instrumental and chemical influences. Chemically,

methods may experience limited reagent capacity, inconsistency of recovery at higher analyte concentrations and depressed recovery in the presence of other species. Instrumentally, there are few limitations at the upper limit when considering the range of analyte masses (0-100 μg) of concern to this study.

The sensitivity is very much governed by chemical and spectroscopic factors. Sensitivity in the context used here is defined in units of x-ray counts per second per μg analyte element ($cps \cdot \mu g^{-1}$). The recovery of an element has a direct effect upon the amount of material irradiated and the effect of this is serious but obvious. The matrix in which the element is bound will influence sensitivity as will the instrumental parameters for the two spectrometer types used:

Energy dispersive x-ray spectrometer. The main parameters controlling sensitivity are anode material, tube voltage and current, and primary filter characteristics. Providing these parameters are standardized then the mass absorption coefficient of the analyte element at the effective excitation energy of the source governs overall sensitivity. Thus, the lower in energy the element analytical line absorption edge lies below the excitation energy the lower is the sensitivity (for the same spectral series).

Wavelength dispersive x-ray spectrometer. The parameters are similar in this case but the ability to influence sensitivity of any one element is increased by greater instrument flexibility. In particular, the choice of analyzing crystal and detector type along with the higher x-ray tube powers obtainable and the higher input count rate tolerance usually result in higher sensitivity and extended linear range for this instrument when compared to EDXRF. Inevitably, the sensitivity influences the LLD, thus, the higher the sensitivity, then, usually the lower the LLD.

The reproducibility of a method is reflected in the percent relative standard deviation (%RSD = $S/\bar{x} \times 100$) of replicate determinations. The level of this determination must be consistent for all methods and has been standardized to 300 ppb in this instance. All other factors being equal, the lower the %RSD the better the method. In particular, the %RSD of blank determinations governs the LLD of a method as discussed earlier. The reproducibility generally deteriorates with each stage of sample handling and each of these increases in %RSD is difficult to predict. Spectroscopically, the actual precision is governed by well-defined statistics of counting and can be predicted. Overall method reproducibility is better obtained experimentally by replicate determinations and will incorporate all effects into the figure of merit obtained. This overall method %RSD yields a figure more amenable to an intermethod comparison study. The three analytical criteria/figures of merit have been determined for each method and element using both wavelength and energy dispersive x-ray spectrometric techniques. The results of these single element/method evaluations are collected in Appendix C. In this table, the general trend of higher WDXRF sensitivity is seen, but it may be better to treat the figures of merit method by method.

Chelation with 8-hydroxyquinoline and Adsorption on Activated Carbon (AC)

The ability of oxine to recover several elements from aqueous solution is well-known, as is its inability to recover As(III) and Se(IV). This behavior is again seen in the results of this study. Sensitivities ($cps \cdot \mu g^{-1}$) using EDXRF are generally low due in part to the low tube current employed (200 μA) and made necessary by the large amount of scatter from the sample. The low sensitivity for Sb and consequent high LLD are due to the enforced use of the $L_{\alpha 1}$ emission line which is very inefficiently excited using silver K_{α} irradiation. The more-generally low sensitivities (EDXRF) for the other elements may be attributed to two factors. Firstly, the complexed metal is diluted by the activated carbon and secondly, the relatively low atomic number carbon matrix causes increased scatter yielding decreased detectability. This generally poor sensitivity is also reflected to some extent in the relatively high %RSD figures and the latter are compounded by problems of sample handling. The much higher x-ray sensitivities to be gained by the use of WDXRF yield better overall performance. Despite this advantage, the %RSD remains high using WDXRF, thereby reflecting the handling difficulties experienced with the rather intractable activated carbon adsorbent.

Precipitation with Ammonium pyrrolidinedithiocarbamate (APDC)

All the elements considered with the exceptions of Cr(III), Mn(II), and Tl(I) were recovered. Cr(III) is largely inert due to the stability of $Cr(H_2O)_6^{3+}$ species, while Mn(II) complexes are particularly unstable and Tl(I) complexes are soluble (28). EDXRF sensitivities are good for all elements except Sb(III) (poor excitation of the L_{α} emission line) yielding LLD values of approximately 0.3 μg (3 ppb) and %RSD values ≤5%. WDXRF data are similar with slight benefits through the range resulting from increased x-ray sensitivity. This latter advantage is reflected in the generally good %RSD figures. In addition to the analytical advantages outlined above, the method is attractive in its simplicity, lack of practical problems, and availability of reagents.

Chelation with Immobilized Dithiocarbamate (CPG)

Using EDXRF the CPG method yielded even lower sensitivities than the AC method. Firstly, only 200 μA x-ray tube current was used as the low atomic number matrix caused a large amount of scatter thereby generating high dead times at the 300 μA tube current normally used. Secondly, the glass matrix dilutes the sample and generates high background which leads to the reduced sensitivity and to decreased detectability, respectively. Additionally, the sample is becoming relatively thick while the presence of surface coating alone causes effective volume and mass dilution of the analyte. The different elements recovered using CPG when compared to methods using dithiocarbamate precipitation might be explained in the following ways:

(a) Cr(III) is generally not recovered at all by dithiocarbamates. Its recovery by an immobilized dithiocarbamate may be a result of factors not directly influenced by the immobilized group itself.

Thus, at the high pH on the column (pH = 8) significant hydrolysis of the trivalent chromium ion is to be expected. Such hydrolyzed species may easily be adsorbed onto the unreacted/exposed surface of the siliceous substrate (29). In addition to this, the pH is sufficiently high to form Si-O groups on the glass surface which may themselves complex Cr species.

(b) Mn(II) is also not usually recovered by dithiocarbamates but, as in the case of Cr(III), extensive hydroxide formation is to be expected at pH 8 and subsequent adsorption of such species onto the support will yield a measurable Mn recovery.

(c) The high pH of complexation may also explain the surprising lack of recovery of both As(III) and Se(IV) as it has been noted (30) that neither As(III) nor Se(IV) are recovered at pH $\geq$ 5.5 by dithiocarbamates.

(d) The relatively low recovery of Cu(II) may also arise from high pH as it is reported (30) to be difficult to form Cu(II) dithiocarbamates at a pH $\geq$ 8.

(e) The recovery of Tl(I) by the immobilized dithiocarbamate is not surprising. Usually Tl(I) complexes are soluble (28), but the immobilization of the reagent clearly removes the possibility of complex elution.

Using EDXRF, sensitivities and, therefore, limits of detection are poor with LLD figures in the region of 20/30 ppb (100 mL sample). The low sensitivities accompanied by the difficulties of handling tend to result in poor (high) %RSD values in the range 10-20%. Using WDXRF all the figures of merit are proportionately improved due to enhanced sensitivity, but these improvements are not as large as might be hoped for.

Precipitation with Sodium Dibenzyldithiocarbamate (DBDTC)

All the elements considered, with the exception of Cr(III), are recovered using the DBDTC precipitant. An advantage of DBDTC over other dithiocarbamates is the recovery of both Mn(II) and Tl(I). One is led to assume that the Mn-DBDTC precipitate is more stable than that for other dithiocarbamates and that the Tl-DBDTC complex is not soluble in this instance. Using EDXRF, sensitivities are generally good resulting in LLD values <0.5 μg (5 ppb) for almost all the elements considered. Additionally, method precision is good as indicated by the low percent %RSD figures ($\leq$5%). Data obtained using WDXRF are similarly good with a slight improvement in sensitivity, leading to lower LLD values and precision usually better than 5% relative. The method has all the other advantages of APDC with the exception of commercial availability of the reagent.

Precipitation with Sodium Diethyldithiocarbamate (NaDDC)

Of all the dithiocarbamate reagents used, NaDDC recovered the least number of elements. Neither Cr(III), Mn(II), nor Tl(I) are recovered--for

the same reasons as discussed for APDC. The inability of the reagent to recover either As(III) or Se(IV) is less explicable and was entirely unexpected. Using EDXRF all elements showed good sensitivity due to the very thin precipitate films formed. Sb(III) showed low sensitivity and high LLD for reasons discussed earlier, whereas Zn(II) showed poor and variable recovery reflected in low sensitivity, high LLD, and poor reproducibility. Precision was, in general, approximately 5% relative for the K_α lines but was higher for the L_α analyte lines (Sb, Hg, Tl, and Pb). Using WDXRF a similar performance was observed with little or no advantage to be gained, indicating the method constraints to be of a chemical rather than spectroscopic nature.

Precipitation with Poly(vinylpyrrolidone) and Thionalide (PVP-T)

Of all the methods considered, PVP-T recovered the least number of elements--only 6 of the 15 studied. Previous reports indicated more elements to be recovered; however, this was found not to be the case in this study even after attempts by several people and after consultation with one of the original authors (12). Thionalide has suitable vacant orbitals on the sulfur atom such that back-bonding from the coordinated metal is possible and, indeed, preferred. Thus, metals with filled d-orbitals (i.e., not transition metals) are favored for bonding with the ligand. Of the first transition series only Cu(I) is expected to form complexes on the basis of the above criterion. Of the elements which we might expect to form stable complexes (Ag, Cd, Hg(II), Tl, Pb, As, Se, and Sb), only Cd, Sb, and Tl were found not to do so. The presence of PVP appears to change little of these thionalide properties. In general, the sensitivities for the elements which were recovered was low for both x-ray spectrometric methods and is the result of two effects. Firstly, the need to filter the precipitates through a 47-mm-diameter filter and then cut this down to fit a 32-mm sample holder resulted in the discarding of a large amount of analyte material. Secondly, the recovery of some elements was frequently less than quantitative--though reproducibly so. Largely due to these low sensitivities the LLD figures are high (≥20 ppb). Observed %RSD figures are, for both instrumental finishes, similar and range from 3-20% relative--the majority of the imprecision arising from sample handling.

Collection on Cation-Exchange Resin-Impregnated Filter Papers (SA-2)

The strong acid cation exchanger used in this filter paper was able to preconcentrate all the elements considered which exist as cations in solution. Thus, elements existing as anions in aqueous solution (As(III), Se(IV), and Sb(III)) were not recovered. Using EDXRF, sensitivities were good with the exception of Hg (0.22 cps/μg) leading to LLD figures usually less than 0.5 μg (<5 ppb). Precision (%RSD) was generally in the 5-15% relative region except for Hg whose low sensitivity tended to result in poor performance generally. Using WDXRF, sensitivities were, as expected, improved. However, little improvement in precision was seen and this tended to raise LLD figures to higher values than would be hoped for on the basis of sensitivity alone. Thus, a large body of response data for each of the method/element/instrument combinations were produced. This body of data will be used to enable an objective assessment of the "best" method on the

basis of the above response criteria (Section Overall Evaluation and Optimum Preconcentration Method).

INTERFERENCE STUDIES

The effects of interferents upon the methods were assessed by means of a two-level factorial (25,26) experimental design. This factorial procedure was used in preference to a "one-factor-at-a-time" design as the former afforded greater economy with somewhat better representation of real samples containing several potentially-interfering concomitants (27). A lower level of interferent concentration equal to zero (i.e., absence of interferent species) was chosen, whereas the higher level was selected to reflect a reasonable environmental level of interference. Thus, the interference evaluation was conducted at a level of analyte of 20 μg (200 ppb) with the interferents Cr(III), Mn(II), Fe(III), Co(II), Cu(II), Zn(II), Pb(II), and Cd(II) in a five-fold excess (1 ppm). Sodium chloride was present at 0.5% m/v and calcium at 100 ppm. These elements and levels were chosen for their approximation to levels anticipated in water samples. Interferences were compared using spectra collected using energy dispersive x-ray spectrometry (EDXRF) except in the cases of Ag and Cd where wavelength dispersive x-ray spectrometry was used through necessity. Figures of merit were produced for each method and element/interferent interaction and were expressed as percent enhancement or suppression of the observed 200 ppb pure element signal.

General trends are observable also in this part of the study, but the complexity of the possible interactions makes some interpretations particularly difficult. However, one prevalent effect which is explicable and large is that of neighboring element spectral interference. This may occur in two possible ways, both of which are severe, but which give rise to effects of opposite sign (+ = enhancement, - = suppression). The possibilities in the case of Mn are seen in Figure 1.

Figure 1a shows the effect of the CrK_β peak on the analyte MnK_α peak. The five-fold excess of Cr over Mn guarantees a large enhancement of the analyte signal. Typically, the K_β intensity is 13% of the K_α intensity for Cr, Mn, and Fe such that 100 μg of Cr will give an effective Mn peak enhancement equal to 13 μg (or 165% of expected). The other effects of neighboring spectral lines are due to the choice of energy windows for the peak above background integration of the analyte K_α (or L_α) peak. If these windows are chosen in absence of interferent then the effects shown in Figures 1b, c, and d may give rise to suppression of the analyte peak (hatched area). These effects presuppose that the background is computed on the basis of a straight line drawn from the low to the high energy limit of the window. As the energy window is made wider, the neighboring peaks from the interfering elements (5 × more intense than the analyte peak) begin to appear in that window and the "baseline" is no longer computed from the true background on either side of the analyte peak, but now include some part of the neighboring interferent peaks. As an example, it is possible that a depression of the Mn peak may be caused in this manner when the low energy limit of the integration window is wide enough to include a portion of the CrK_α peak.

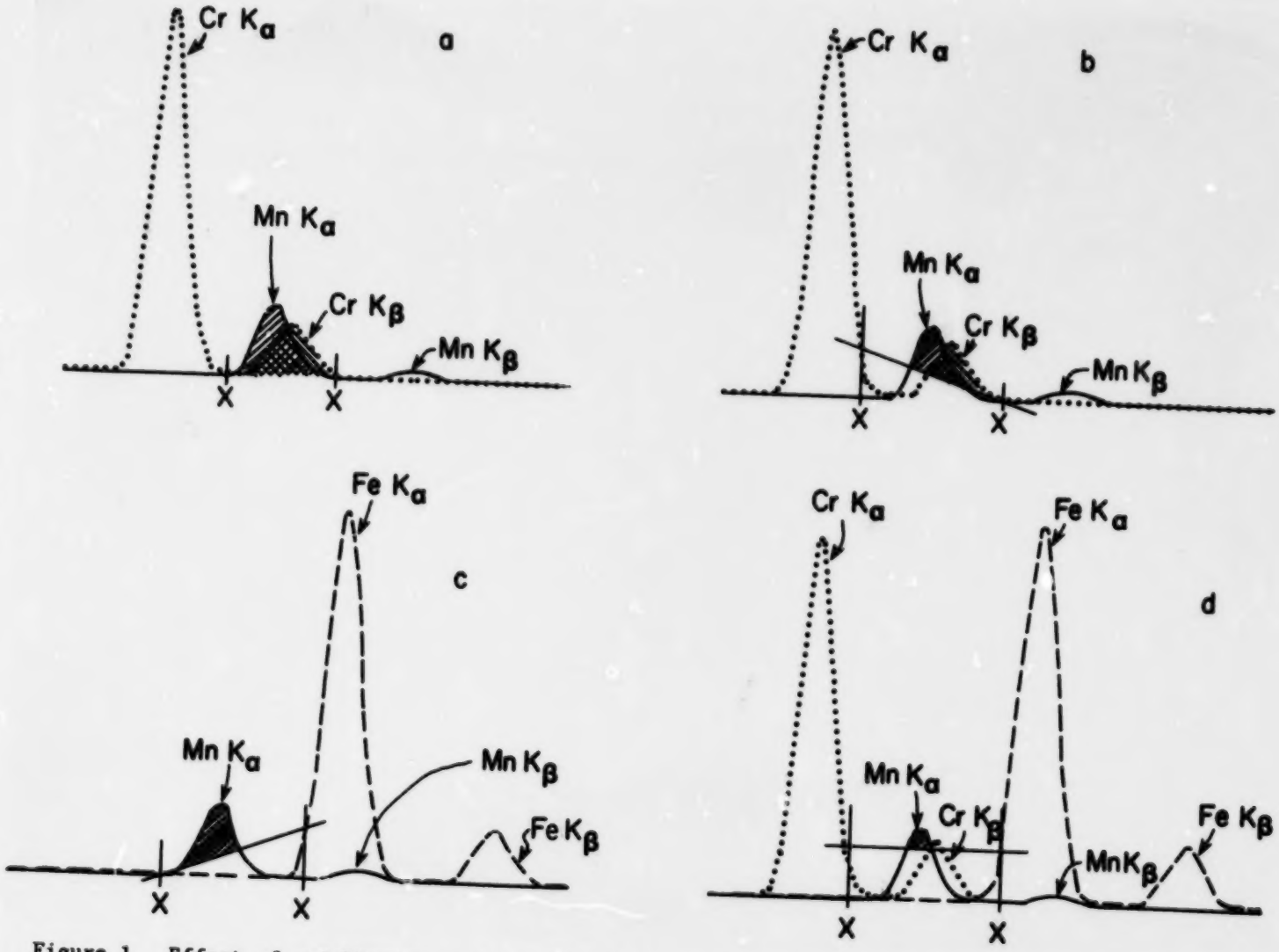

Figure 1. Effect of neighboring peaks. (a) Effect of Cr_{β} on MnK_{α} (enhancement); (b,c,d) effects of neighboring peaks on the integral MnK_{α} peak above background with varying energy windows. x ——— x.

There is a further special case of spectral enhancement when Pb and As are present together. X-ray fluorescence spectra containing the AsK_α and PbL_α peaks show direct peak superposition and enhancement effects are expected to be severe. Thus, we expect to see the AsK_α/PbL_α enhancement along with several neighboring K_α/K_β enhancement or adjacent K_α/K_α suppressions for the first row transition elements. There are, of course, other possibilities for spectral interaction and these will be discussed as they arise. Spectral interferences will be compounded with chemical effects (and vice versa) in some instances, but in all cases it would seem better to discuss the observed effects method by method.

Chelation with 8-hydroxyquinoline and Adsorption on Activated Carbon (AC)

When using this method, four elements (Co, Ag, Cu, and Hg) were unaffected by any of the interferents whereas As(III) and Se(IV) were not recovered by oxine (TABLE D-1, Appendix D). Of the interferents, NaCl and Ca both suppressed the observed Fe signal. Several interferences (Mn/Cr, Fe/Mn, Ni/Co, Ni/Cu, Zn/Cu, and Sb/Cd) were observed all of which can be explained in terms of one or more of the spectral factors outlined earlier for $Z \pm 1$ interactions. Co(II) exerted a depressive effect on many analyte elements which may have been a result of the particularly effective complexation of Co(II) by oxine leading to some reagent deficiency for the analyte. Those elements for which the highest %RSD figures were observed tended to show the largest number of interferences (e.g. for WDXRF %RDS values: Fe = 11.7; Cd = 14.8; Sb = 12.6; Hg = 9.5; and Tl = 10.7). This perhaps indicates that those elements whose recovery is not very stable in pure solution suffer even wider variation when interferent species are present in excess.

Precipitation by Ammonium Pyrrolidinedithiocarbamate (APDC)

Cr(III), Mn(II), and Tl(I) were not recovered using the APDC precipitant and Pb(II) was unaffected by all interferents (TABLE D-2). Of the observed interferences the largest numerical values were, for instance, where spectroscopic interference was expected (Fe/Co, Co/Fe, Ni/Co, Cu/Zn, Zn/Cu, As/Pb, and Sb/Cd). In the Sb case there is the possibility of overlap/interference with the SbL_α by the CdL_β line. Of the other interactions, Cu showed most interference but the variation for all the mainly "chemical" interferences was small suggesting the method to be generally effective under the conditions studied.

Chelation with Immobilized Dithiocarbamate (CPG)

Using the CPG method neither As(III) or Se(IV) are recovered and the elements Cr, Cu, and Ag show no influence from any of the interferents studied (Table D-3). Nine possible spectroscopic effects were observed (Mn/Cr, Fe/Mn, Fe/Co, Co/Fe, Ni/Co, Ni/Cu, Zn/Cu, Sb/Cd, and Tl/Pb) and, as expected, these interactions were of a large magnitude. Many interferences are noticeable in this method, several of which are largely inexplicable except to note that the method precision (as reflected and expressed in the %RSD) is generally poor. Thus, Fe with a %RSD at 300 ppb of 24.2% (WDXRF) suffers from seven out of nine possible interferences and, in general, the

imprecision of the method does not lend it to more detailed or exhaustive investigation.

Precipitation with Sodium dibenzyldithiocarbamate (DBDTC)

The DBDTC method did not recover Cr(III) and the elements Zn, Se, Ag, Cd, Sb, Hg, and Pb were unaffected by the interferents studied. Of the interferents, salinity (NaCl), Ca, Cr, Mn, and Cd showed no effect. This is to be expected for Cr(III) as it is not itself recovered and, thus, will be unable to interfere either chemically or spectrally. Of the few remaining observed interferences (TABLE D-4) several may be due, in part at least, to spectral interference (Mn/Fe, Fe/Co, Co/Fe, Ni/Co, As/Pb, and Tl/Pb). The remaining five effects may be explicable from a mainly chemical standpoint. In the case of Co interference the scavenging of reagent by the excess Co interferent appears to result in depression of recovery for a few elements. The problem of reagent competition/scavenging is best seen with Mn as analyte where Co, Cu, and Zn are found to cause a suppression in the Mn signal. This particular chemical suppression can be eliminated by doubling the amount of precipitating agent added. On doing this, the only interference is from Fe which depresses the Mn signal 27% and may well be due to spectral proximity as discussed earlier. The reason for Mn exhibiting the most severe chemical interferences (depression) is thought to lie in the difficulty of formation of the Mn-dibenzyldithiocarbamate which will be even more difficult in the presence of interferent excesses.

Precipitation with Sodium Diethyldithiocarbamate (NaDDC)

Five elements (Cr, Mn, As, Se, and Tl) were not recoverable using NaDDC (TABLE D-5) and of the rest, the interferences were few and generally small (<10% deviation from expected). Three possible spectral interactions were observed (Fe/Co, Ni/Co, and Sb/Cd) the remaining interferences being due to chemical interactions which are difficult to explain. There was little or no interference from the macro-elements (Na and Ca) indicating the general utility of this method in natural water analysis.

Precipitation with Poly(vinylpyrrolidone) and Thionalide (PVP-T)

The PVP-T method (TABLE D-6) recovered the least number of elements of all the methods considered, showing no response for nine elements (Cr, Mn, Fe, Co, Ni, Zn, Cd, Sb, and Tl). Despite this poor overall performance the number of observed interferences was low with Ca, Cr, Mn, Fe, and Cd having no effect on any of the recovered elements. Of the observed interferences, two (Cu depression by Zn, and As enhancement by Pb) are explicable spectroscopically. The interference on Se is not easily understood whereas the enhancement seen for Pb may well be due to the lack of precision (20% %RSD at 300 ppb using WDXRF) observed for that element.

Collection on Cation-Exchange Resin-Impregnated Filter Papers (SA-2)

Three elements (As, Se, and Sb) were not recovered using the cationic resin for reasons outlined earlier. Mn did not interfere with any of the elements studied, but the remaining interferences were numerous (TABLE D-7).

Of these interferences four may be attributable to spectral effects (Mn/Cr, Ni/Co, Zn/Cu, and Tl/Pb). The most widespread interferent effect was shown by calcium. Almost all the elements exhibited markedly depressed analyte signals (i.e. decreased recoveries) caused by depletion of ion-exchange capacity. Thus, in the presence of 100 mgL^{-1} calcium ion the cationic resin exchange sites are rapidly taken up by the large excess of calcium (which, being a dipositive ion, is strongly exchanged from solution) leaving the analyte ions in the filtrate liquor.

In general, therefore, the observed interferences upon the methods are explicable. However, several effects cannot be explained on the basis of first order interactions. Thus, some of the observed effects may well be due to second, or indeed higher, order interactions. Alternatively (and additionally) the large relative standard deviation seen for several elements may not lend certain element/method data to extensive statistical evaluation. Despite these latter two points, the two-level factorial experimental design has shown itself capable of identifying many potential interferences which are explicable and, indeed, expectable using the experimental design and instrumental parameters described. It is important also to realize that, through the use of a spectral deconvolution routine, the effects of spectroscopic interaction, e.g., As/Pb overlap, can be minimized or, in most cases, removed entirely, leaving only the chemical interferences to evaluate and correct.

EFFECT OF NATURALLY OCCURRING ORGANIC MATERIALS

Pilot Study

Initially, it was necessary to identify the type and magnitude of the effect of humic materials upon the preconcentration methods. Thus, five replicate determinations were made for each of the ions Co(II), Cr(III), Cu(II), Zn(II), Fe(III), Hg(II) and Pb(II) using all of the preconcentration methods described above with the exception of DBDTC. Three solutions containing 200 $\mu g\ L^{-1}$ metal ion alone, 200 $\mu g\ L^{-1}$ metal ion + 9 $mg\ L^{-1}$ humic acid, and 200 $\mu g\ L^{-1}$ metal ion + 24 $mg\ L^{-1}$ humic acid, respectively, were employed. The effect of both levels of humic acid upon the sodium diethyldithiocarbamate and ammonium pyrrolidinedithiocarbamate precipitation methods was to form a filter-clogging colloid rendering the methods impractical. The effect of humic acid upon the remaining three preconcentration methods is summarized in Figure 2 in which recoveries of each metal, by each method and for both levels of humic acid are normalized to the recovery of metal in the absence of humic acid. It is noticeable that the method using 8-hydroxyquinoline/ activated carbon is least affected; presumably due to the adsorption onto the activated carbon of any humic-metal complexes along with the oxine complexes (8). The resin impregnated filter paper shows proportionate lowering of recovery at the two levels of humic acid for all ions except Pb(II), suggesting formation of non-exchangeable metal-humic complexes in the case of most ions. The controlled pore glass-immobilized dithiocarbamate method was found to exhibit significantly decreased recoveries ($\leq$ 30% relative) for all elements. This decrease may result from the formation of metal-humic complexes and/or from coating of the silylated surface

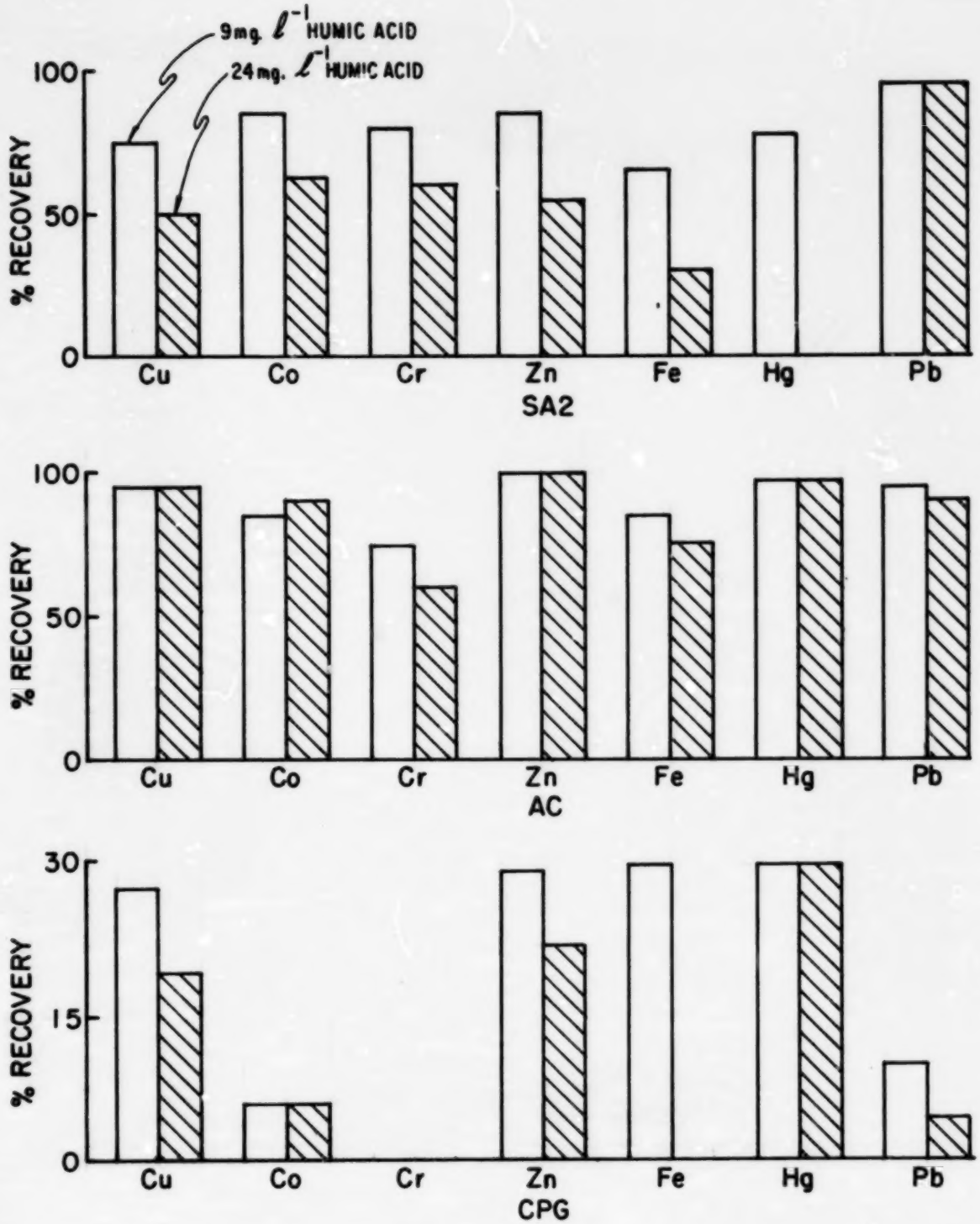

Figure 2. Percentage recoveries of Cu(II), Co(II), Cr(III), Zn(II), Fe(III), Hg(II), and Pb(II) in the presence of 9 and 24 mg/L^{-1} of humic acid. (A) Ion-exchange resin impregnated filter paper; (B) Oxinate adsorption on activated carbon; (C) Dithiocarbamate immobilized on controlled pore glass.

by adsorption into or plugging of the pores. It may be concluded from the pilot study that humic material interferes with the preconcentration of most ions investigated and that methods for the removal of this interference must be sought if preconcentration is to be employed using the methods considered.

Methods for the Elimination of Humic Interferences

Three methods for eliminating humic interference prior to metal concentration were considered. These were adsorption on activated carbon (8), wet oxidation using either dichromate (31), permanganate, or persulphate (32) and photochemical decomposition (33). The use of adsorption on activated carbon creates sample handling difficulties. Use of wet oxidation was also discounted because of chemical inefficiency, sample treatment time, and the inevitably increased blanks arising from reagent addition. Thus, UV irradiation was chosen because no additional reagent is required and rapid degradation of organics with only water and carbon dioxide as by-products is possible. The concentration of total organic carbon of a solution containing both humic and fulvic acids (5 ppm each) as a function of UV irradiation time is shown in Figure 3. Substantial degradation of organic material is achieved after 15 minutes irradiation with the solution adjusted to pH 2. The ability of UV irradiation to reduce the effects attributable to humic materials was investigated using four types of solution:

O containing 200 $\mu g\ L^{-1}$ metal ion only
H containing 200 $\mu g\ L^{-1}$ metal ion + 9 $mg\ L^{-1}$ humic acid
F containing 200 $\mu g\ L^{-1}$ metal ion + 5 $mg\ L^{-1}$ fulvic acid
M containing 200 $\mu g\ L^{-1}$ metal ion + 5 $mg\ L^{-1}$ humic + 5 $mg\ L^{-1}$ fulvic acid.

Each of these solutions contained 200 $\mu g\ L^{-1}$ of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II), Cd(II), As(III) and Tl(I) which were determined first with no pretreatment and then after UV irradiation for 15 minutes at pH 2.

Dithiocarbamate Precipitation--

In the absence of UV irradiation, both sodium diethyldithiocarbamate (NaDDC) and ammonium pyrrolidinedithiocarbamate (APDC) yielded unfilterable colloids in the presence of humic acid and mixed humic/fulvic acid solutions. Fulvic acid alone similarly affected NaDDC, whereas APDC was unaffected for all the ions considered in that case (Fe(III), Co(II), Ni(II), Cu(II), Zn(II), As(III), Pb(II) and Hg(II)). After UV irradiation of the four types of solution, approximately quantitative recovery of all the elements determined was obtained with the exception of As(III). This loss of As(III) upon UV irradiation was independent of organic content and may have been a result of the oxidation of As(III) to As(V) during irradiation. As(V) is not precipitated by either dithiocarbamate.

Dithiocarbamate Immobilized on Controlled Pore Glass--

Severe depression of recovery in the presence of humic material had been encountered in the pilot study and was observed in the extended study as shown in Table 1. Significant decreases of recovery were observed for Cr(III), Mn(II), Fe(III), Cu(II), Hg(II) and Pb(II) when humic, fulvic or both acids were present. Only the presence of the mixed organic solution

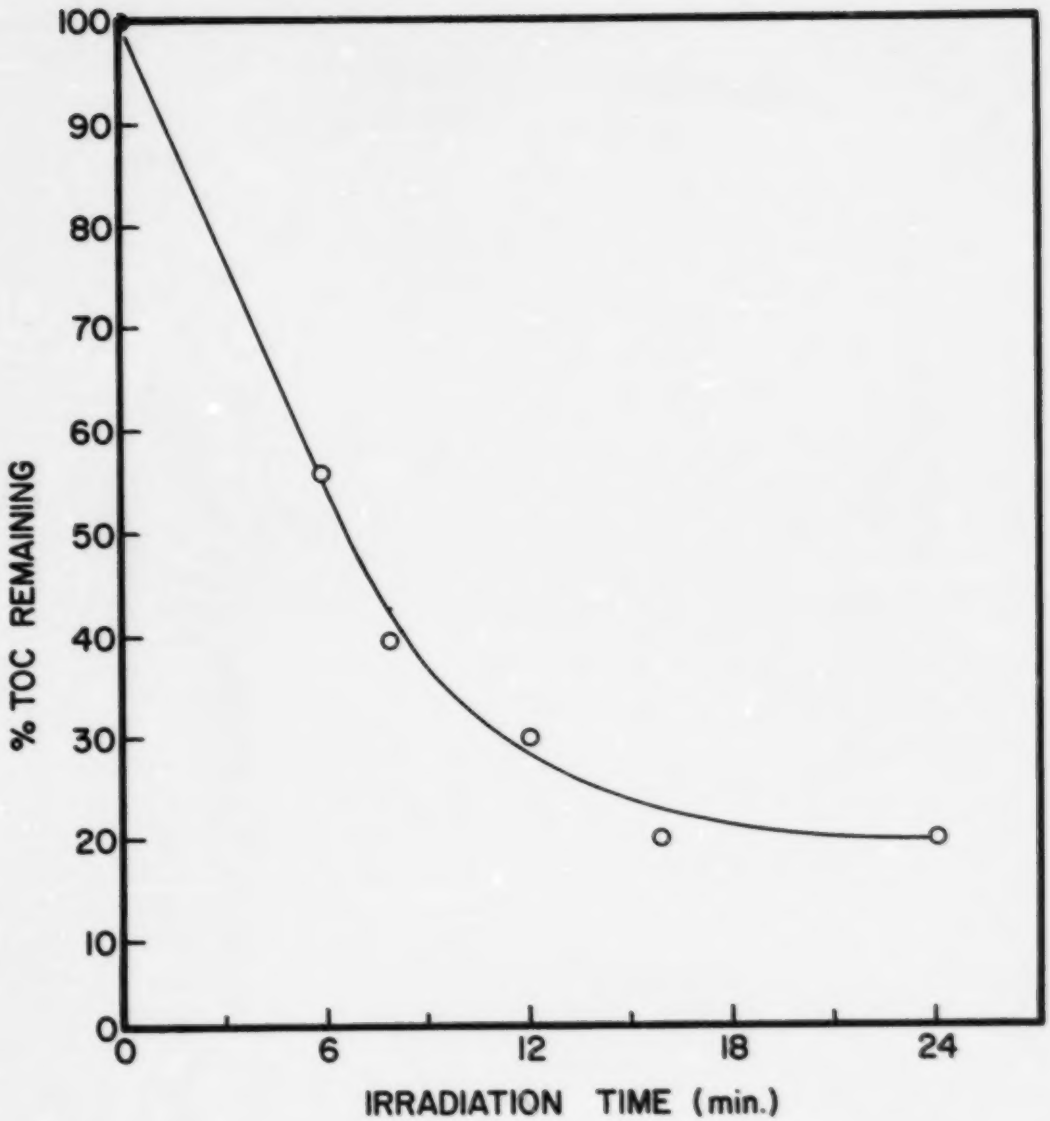

Figure 3. Total organic carbon as a function of UV irradiation time.

TABLE 1. EFFECT OF ORGANICS AND IRRADIATION ON THE RELATIVE RECOVERIES* OF SELECTED ELEMENTS USING PRECONCENTRATION BY THE CPG METHOD*

	Untreated			Irradiated		
	H	F	M	H'	F'	M'
Co	94	97	81	92	96	96
Ni	95	93	75	93	105	93
Zn	96	86	79	104	106	91
Tl	112	99	89	96	99	101
Cu	86	85	66	98	98	97
Cr	31	92	19	93	87	105
Mn	46	72	38	118	83	86
Fe	41	84	27	96	105	106
Hg	52	59	51	97	101	90
Pb	45	69	24	98	101	92

* Relative to identical samples with no added organics (recovery in %).

decreased the recovery of Co(II), Ni(II), Zn(II) and Tl(I) significantly. Without exception, the recovery was restored to nearly 100% after UV irradiation, demonstrating the potential utility of this method for degradation of the organic material.

Ion Exchange Resin Impregnated Filter Paper--

The use of the Ion Exchange Resin Impregnated Filter Paper technique was of limited value on two counts. First, the presence of humic and/or fulvic organic materials showed depressed recovery values for all elements tested with the exception of Pb(II). Second, as described earlier, this technique is one of the most susceptible to interference from concomitant ions. It is especially sensitive to interference from Ca^{+2}.

Complexation by 8-hydroxyquinoline and Adsorption on Activated Carbon--

For the elements considered (Mn(II), Cr(III), Zn(II), Fe(III), Ni(II), Cu(II), Co(II), Pb(II), and Hg(II)) no significant loss of recovery in the presence of humic or fulvic acid or of their mixture was observed. This may be attributed to the adsorption of any metal-humic complexes on the activated carbon (8). Therefore, no advantage would be gained from UV irradiation of

the samples at the levels of organic material considered. The adsorption of both natural organic and oxine complexes may be of disadvantage, however, if speciation information is required.

Effects of Humic Material on Other Spectroscopic Techniques

A parallel study to the one using preconcentration and energy-dispersive XRF was conducted using flame atomic absorption (AAS), d.c. plasma optical emission (DCP/OES) and inductively coupled plasma optical emission (ICP/OES) spectrometry. Aliquots of the four sets of solutions (O, H, F and M) used for the X-ray studies were used for the determination of each element possible both before and after UV irradiation. None of the three methods yielded a significant depression of signal due to the presence of humic materials. No significant variation was found between irradiated samples and those which were not irradiated.

Arsenic

Arsenic is an element whose behavior during irradiation and subsequent determination by EDXRF after dithiocarbamate precipitation was anomalous. Irradiation was found to decrease the recovery to less than 20% of the expected value as shown in Table 2. Results from the analysis of aliquots of the same samples using DCP/OES and ICP/OES show no such decrease as shown in Table 2. From the DCP/OES and ICP/OES results it is clear that total As is unaffected by the presence of humic materials or by irradiation, and therefore is not being lost as a volatile arsenic compound. After irradiation of the sample in nitric acid solution at pH 2, it appears that the As present does not yield a precipitate with the dithiocarbamates. This likely results from the oxidation of As(III) to As(V); the latter does not form precipitates with dithiocarbamates.

TABLE 2. EFFECT OF UV IRRADIATION UPON THE RECOVERY (%) OF 20 μg As BY VARIOUS TECHNIQUES

	Untreated				Irradiated			
Method	Ø	H	F	M	Ø'	H'	F'	M'
APDC EDXRF	100	a	102	a	10	8.5	9.8	6.9
NaDDC EDXRF	100	a	a	a	10.7	21.6	14.3	13.7
ICP/OES	100	96.6	97	95.3	99.2	91.1	94.9	98.7
DCP/OES	100	106	112	108	89	106	102	109

a Forms an unfilterable colloid.

Of several methods available for the preconcentration of trace metal ions prior to determination using EDXRF spectrometry, complexation with 8-hydroxyquinoline followed by adsorption on activated carbon is generally unaffected by humic substances at concentrations of 10 ppm or less. Methods employing precipitation by NaDDC and APDC collection on an ion-exchange resin-impregnated filter paper or complexation by an immobilized dithiocarbamate, on the other hand, show severe loss of efficiency in the presence of dissolved humic material. The efficiency of these methods may be simply and reliably reinstated by UV irradiation of the sample for 15 min at pH 2. Such treatment should alleviate difficulties often encountered in the analysis of natural waters high in humic substances.

OVERALL EVALUATION AND OPTIMUM PRECONCENTRATION METHOD

Much data have been accumulated and it was necessary to generate from these data some form of method assessment to enable a choice of the optimal method to be made. From the foregoing response data (Sec. 5, Response Characteristics), it is evident that each method has its merits and disadvantages. Not only are there merits and disadvantages of a purely objective nature based upon the meeting of analytical criteria but there are those based on more subjective criteria such as convenience, cost and simplicity. The latter are more difficult to assess but the former might be evaluated using a figure of merit derived from assessment of analytical performance. An additional advantage of the 'figure of merit' approach is the reduction of all the response data to manageable proportions. Such a figure of merit has been derived from the response data alone on the basis of the semi-empirical equation (1):

$$\text{Rating, } R = \sum_{i=1}^{n} \ln \frac{(\text{Linear range})}{\sqrt{2\pi e} \times s} \qquad (1)$$

where

n = the number of elements recovered
linear range = upper calibration limit (50 or 100 μg) minus LLD
Standard deviation(s) as determined at 30 μg (300 ppb).

When the response data from Appendix C are evaluated using this equation one obtains the figures of merit shown in Table E-1 (Appendix E).

As would be expected, the method rank is independent of the instrument used. WDXRF yields the widest range of rating values therefore its ability to discriminate between methods may be a little better than EDXRF. On the basis of the ratings in Table E-1 the PVP-T method is clearly the worst, the major reason for this lying in the few elements recoverable. Two of the precipitation methods (APDC and DBDTC) are indicated to be the optimum methods. This is not surprising as these methods reliably concentrate most of the elements of concern and they are particularly "rugged." That is to say, they present no handling problems yielding good reproducibility irrespective of the analyst. The formation of a very thin precipitate film, most of which is placed in the incident x-ray beam, leads to high sensitivities

for these methods. The AC, CPG, and SA-2 methods lie in an intermediate group where the techniques are widely applicable. However, because of either dilution of the analyte (AC/CPG) or poor capacity (CPG/SA-2), they are generally inferior to the dithiocarbamate precipitation methods. In addition, the AC and CPG methods are rather time-consuming, and the AC method has particular handling problems which are reflected in overall poor performance but especially in the lack of precision. Of the dithiocarbamate precipitants, NaDDC is anomolously poor mainly due to its inability to recover several elements. In particular its inability to recover As(III) and Se(IV) is a disadvantage and is somewhat surprising.

On the basis of the interference data (Sec 5, Interference Studies), an attempt has been made to quantify and rank the methods in a relative manner through the use of Equation (2).

$$R_I = \sum_{i=1}^{n} \frac{I}{N} \qquad (2)$$

where I is the percent interference, n the number of elements recoverable, and N the number of observed interferences per element.

Based upon the interference data, ratings are obtained for each method which permit the ranking of the methods as shown in Table E-2. From these ratings it is evident that the precipitation and AC methods show the least interference (lowest R_{IA} values) and that the non-selective ion-exchange methods (CPG/SA-2) yield the highest (i.e., worst) figures, as might be expected. If the data from primary spectral effects are removed and Equation (2) is reused the ratings (R_{IB}) and ranking shown in Table E-3 are obtained. These values of R_{IB} are expected to result primarily from chemical interference effects. These data show little or no change in the overall rank except that AC is now moved below the NaDDC and DBDTC methods and DBDTC now becomes the "best" method. Comparing the ratings in the following manner:

$$\% \text{ Chemical interference} = \frac{R_{IB}}{R_{IA}} \times 100\%$$

we can see the relative contribution from chemical interference (Table E-4). On the basis of these ratings the methods appear to fall into two main groups:

(a) The dithiocarbamate precipitation methods (<50% of interference is attributable to chemical effects)

(b) CPG, PVP-T and SA-2 (where >65% of the interference is attributable to chemical effects).

AC appears to be intermediate between the two groups. Thus, for dithiocarbamates, more than half the observed interference is spectral and can be easily compensated for, or removed, through the use of a peak deconvolution

routine. This is particularly true for the DBDTC method. Removal of the remaining chemical effects (once identified) may require modification of the method or the use of masking reagents where large amounts of potential interferences are known to be present. The remaining methods show increasing amounts of chemical interference thereby becoming less amenable to routine analysis of, for instance, widely varying environmental samples.

On the basis of the above two ranks the DBDTC precipitation method is clearly "best." The recovery of all the elements of interest, with the exception of Cr(III), and ability of the method to withstand chemical interferences combine to make this method attractive and the "best" on the basis of our rating scheme. The APDC and AC methods lie jointly in second place, there being little to discriminate between these two methods. However, the handling inconvenience and time-consuming procedure experienced with the AC method suggest that, overall, the APDC method may be preferred. Despite the high interference rank for the NaDDC method, the few elements recovered yield a low response rating and overall this is the poorest of the dithiocarbamate precipitation methods. Of the remaining three methods (CPG, PVP-T, and SA-2) there is little to distinguish between them and all have low ranks for both response and chemical interference. The SA-2 method has a higher response rank but is subject to a large number of interferences whereas the PVP-T method shows the inverse characteristics. The CPG method has a most consistent, but low, rank. Thus, the overall method of choice from the seven studied is the method using precipitation by sodium dibenzyldithiocarbamate (DBDTC). The APDC method may be considered to be the second best method.

The limitations of both the numerical methods of assigning an overall figure of merit (rating) and the subsequent relative rank must be realized. The equations are not derived from rigorous statistical principles and are based upon the results of this study alone. These methods of rating may be no more widely applicable than to this particular case in point. It is notable, however, that the numerical ratings and the accompanying ranks are in general agreement with the subjective consensus of the experimenters involved. Attempts to extend this method to the numerical evaluation of data from other multielement studies should be regarded with due caution.

CHARACTERIZATION AND APPLICATION TO REAL WATER SAMPLES OF THE OPTIMUM METHOD

Multielement Method Calibration

The multielement calibration of an analytical method is not without its attendant difficulties. For instance, the compatibility of the various elemental standards is not always good. In the case reported here, the admixture of Cr(VI) solutions with those containing Ag(I) or Pb(II) yielded some precipitation (of the chromate). In addition, those standards whose preparation required the use of some HCl in addition to the preferred HNO_3 yielded precipitates (of AgCl) on admixture with silver solutions. Also, some element standards were prepared from the chloride, and, thereby, caused some AgCl precipitation, too. Thus, when precipitating for the production of multielement calibration standards, using the dithiocarbamates, two

multielement standards were prepared in order to eliminate the above detrimental effects. In this manner, one multielement standard was precipitated and stirred for 1 minute before addition of the second standard, which contained potential interferences to the first. This method proved to be very successful and overall performance was independent of which of the two standards was added first.

The calibration data obtained by the DBDTC method for all the elements considered are shown in Table F-1. These data are the slope of the calibration line (x-ray counts/sec/μg) the intercept (μg analyte), and the correlation coefficient (R). The x-ray counts are the integral net fitted peak above background counts for the combined K_α/K_β or L_α/L_β peaks as computed using "Super ML." The calibration constants are for a straight line fitted to the 20 data points for each element as computed by "Regal". The analysis of 20 precipitates yielded calibration data for all the elements shown. As may be seen (Table F-1), x-ray sensitivities when using the thin film precipitates are high (>3 cps/μg). For the elements excited by the silver anode characteristic tube emission the sensitivity increases with atomic number or as the element K or L absorption edge more closely approaches the Ag K exciting line emission. Intercepts were generally zero except in the cases of Fe, Cu, and Zn. The largest intercept (+ 1.5 μg) was found for Fe and was due primarily to a reagent (particularly acids) blank but also, to a lesser extent, the spectrometer construction materials. Although the blank level is comparatively high, constancy of reagent addition coupled with the constant spectrometer background meant that the blank was reproducible and did not affect the obtainable limit of detection greatly. In the case of Cu, the small intercept was contributed to by both a reagent blank and a spectrometer blank but both were small and reproducible. In the case of Zn, the positive intercept arose in part from the ubiquitous presence of Zn in reagents, but apparently more seriously, from Zn in the sample mounting cups. Within any one batch of sample cups the Zn content was stable (but not necessarily low) but the batch to batch source of variation of Zn was serious. This gave rise to large variations in the blank, thereby raising the attainable limit of detection unless sample cup batches were carefully matched for Zn content. The elements whose higher energy K and L series emission lines were used exhibited slightly larger blank deviations and this may be attributed to the increasing background in this region of the spectrum. Calibrations for Pb also exhibited high positive intercepts due to the raised Pb levels present in reagents, particularly acids. As acids of the highest purity ("Ultrex") available were used, the magnitude of the blank must approach, but will seldom reach zero, but its reproducibility must be controlled by maintenance of consistent acid volume additions during pH adjustments. As might be expected, very similar data were observed when using APDC as precipitant (Table F-2). Sensitivities (cps/μg) were very similar in all cases except chromium. The same comments upon intercepts/blanks apply to both methods equally. In the case of lead, APDC yielded a higher blank and frequently yielded a somewhat lower correlation coefficient. In general, however, the two methods show very similar calibration behavior.

Elemental Recoveries

The recovery of elements from solution using the DBDTC precipitant (Table F-1) was extensive in range and quantitative at pH 4. The reagent used in this study precipitated both Mn(II) and Tl(I) successfully in addition to Cr(VI). Previous work (7,34) had indicated that Cr was not recovered by DBDTC, but this may be attributed to the use of Cr in the +3 oxidation state. Cr(III) is not recovered by the reagent used in this investigation; however, recovery of Cr in the +6 oxidation state is quantitative at pH 4. In addition, As and Sb in the +3 and Se in the +4 oxidation state only are recovered.

Some notable variations occur in the case of APDC precipitation (Table F-2). Firstly, it is noticeable that neither Mn(II) or Tl(I) are recovered using this precipitant. Reasons for this behavior are thought to lie in the fact that Mn-APDC complexes are particularly weak and that Tl(I) complexes are water-soluble. In the case of DBDTC, the Mn complexes are assumed to be stronger and the use of methanolic solution may yield less-soluble Tl(I) precipitates. Secondly, the sensitivity (cps/μg) for Cr using APDC precipitation is much depressed (0.78 cps/μg) when compared to that observed when using DBDTC precipitation (3.1 cps/μg). Thus, recovery of Cr(VI) by APDC is far below 100%. However, in cases where large (100 μg) amounts of Fe(III) were present, recovery of Cr approached 100% due to the co-precipitation of Cr with $Fe(OH)_3$ hydrates. In addition to the variable, and often low, recovery experienced with Cr when using APDC, similar effects were sometimes observed for Zn and Pb. In these cases, the presence of large excesses of other elements (especially Cu) tended to reduce recovery of Zn and Pb below the normally quantitative level. In general, the recovery of elements when using DBDTC was superior and led to better linearity of calibration, higher calibration slopes and improved precision when compared with the APDC precipitant.

Analysis of Certified Reference Materials

Several secondary certified reference solutions (CRM) were obtained (Appendix B) and analyzed in order to assess the accuracy and precision of the proposed methods. The number and concentrations of elements ranged from five to twenty and from 0.4 to 800 ppb (μg L^{-1}), respectively. Results from the analysis of four such solutions using APDC precipitation are presented in Table F-3. Analysis of ERA 1916 (Waste Water) indicated the ability of the method to determine the elements Se, Cu, Fe, Ni, Co, Hg, and Pb with an accuracy in the region of 5% relative over a range extending from less than 20 to more than 400 ppb. The disagreement of the experimental value for Hg with the certified value was the most severe disparity. However, analysis of the same sample by an independent commercial laboratory using cold vapor AAS showed good agreement with the observed APDC/EDXRF experimental value suggesting the certificate value to be incorrect. The ability of the precipitation/EDXRF method to reliably determine less than 10 ppb mercury is demonstrated by the Hg values determined in samples ERA 1512, EPA 2 and EPA 3. A working lower limit of detection for the analysis of Hg in a 100 mL sample would appear to be 2 ppb which is equivalent to 0.2 μg Hg in the precipitate. Similar accuracy was observed for Se, Cu, Fe, Ni, Co, and Pb.

Serious deviations of the APDC/EDXRF experimental values from the certified values for the elements Zn, Cr, and As were observed. The problems of Zn determinations using APDC in the presence of large and varying amounts of other elements have already been mentioned. In the analysis of Certified Reference Materials severe depression (approximately 40%) of Zn recovery was encountered and this is attributed to the poor (relative) precipitation of Zn by APDC in the presence of the other elements in the sample. Modification of the method by a change in pH or use of a mixed precipitant may well circumvent this problem. In the case of chromium there appear to be two distinct effects. The high Cr value observed in the analysis of ERA 1916 may be a result of enhanced Cr recovery due to co-precipitation in addition to APDC precipitation. The remaining three Certified Reference Materials show no measurable Cr recovery and it may well be assumed that Cr is present in these samples in the +3 oxidation state, which is not measurably precipitated by APDC. The conditions for co-precipitation of Cr(III) are not encountered in these Certified Reference Materials so the observed recovery is zero. Arsenic recovery from ERA 1916 is around 25% and for the remaining three Certified Reference Materials is zero. The conclusion to be drawn in this instance is that ERA 1916 contains a mixture of As(III), which is recovered by APDC, and of As(V), which is not recovered, and that the remaining Certified Reference Materials contain arsenic entirely in the +5 oxidation state. As the reference solutions contain nitric acid as preservative and solvent, the preponderance of As(V) over As(III) is to be expected. Thus, the analysis of the above CRM solutions shows that APDC precipitation coupled with EDXRF is capable of the accurate simultaneous determination of the elements Se, Cu, Fe, Ni, Co, Hg, and Pb at ppb levels in solution. There are some problems in the analysis of the elements Zn, As, and Cr due to inconsistent recovery or oxidation state complications, but simple modification of the method may yield reliable quantitative data for these elements also.

As discussed earlier, sodium dibenzyldithiocarbamate (DBDTC) had shown various advantages in the number of elements recoverable and in the consistency of that recovery. This behavior is again seen in the analysis of ERA 1916 (Table F-4). Thus, the elements Co, Cu, Fe, Pb, and Se are recovered yielding values accurate to ±5% or better of the certificate value. In the case of Hg and Ni these values are 12% and 8% respectively. It is also notable that DBDTC recovers Zn, Tl, and Mn, the former two with excellent accuracy, but the latter with some reduced recovery. In addition to the determination of the above elements, V and Ti were also determinable with high accuracy in this CRM using DBDTC. As had been observed in the case of APDC precipitation, low recoveries were also observed for the precipitation of Cr and As using DBDTC. It is similarly concluded that mixed oxidation states are present giving rise to reduced recovery as only Cr in the +6 and As in the +3 oxidation state are recovered using DBDTC.

Similar behavior is also seen in the determination of the elements Se, Hg, Pb, As, Fe, and Mn in five other CRM solutions (Table F-5). Duplicate values from the determination of the six elements are in excellent agreement with the certificate values for all the samples. The values for Se are particularly good considering the low levels of determination of that element. Thus, Se is determined accurately (better than ±10% relative) even

at a concentration of 5 ppb ($\mu g\ L^{-1}$) in a 100 mL sample. The data for Hg suggest a working lower limit of detection (in the multielement mode) of 2 ppb from a 100 mL sample. However, at a level of 4 ppb a reliable determination may be performed to within 20% relative accuracy. The data for As again show the specificity of the reagent for As(III) in the presence of As(V). Thus, CSL 2291 contained mixed As(III) and As(V) whereas the remaining four Certified Reference Materials contained solely As(V) and yielded no measurable As signal. The determination of higher levels of Fe and Mn is shown in two of the samples (ERA 1512, 1615), indicating high accuracy for Fe determinations at a level of 0.5 ppm. In addition to the excellent Fe data, the ability of DBDTC to accurately and quantitatively recover Mn in these two samples is apparent, making the use of DBDTC precipitation particularly attractive. The foregoing data indicate the ability of both precipitating agents to preconcentrate trace levels of several elements from aqueous solution. The use of DBDTC yields generally more-stable recoveries with the additional benefit of more elements recoverable. The use of EDXRF enables the resulting precipitates to be analyzed with an accuracy better than ±5% in the region extending from 10 to 500 ppb from a 100 mL sample. We have further evaluated the accuracy and precision of the DBDTC/EDXRF method in order to assess the feasibility of its application to real water analysis.

Accuracy and Precision

The overall expectable accuracy and precision of the DBDTC/EDXRF method has been assessed using CRM solutions. Thus, 8 replicate precipitates were produced and analyzed for each of three samples. Two of the samples contained very low levels (usually less than 10 ppb) of several elements (Table F-6); one (Table F-7, EPA 3) contained typical trace element levels. All the samples were analyzed using simultaneous detection and peak deconvolution and the accuracy and precision is on the basis of the total analytical scheme thereby including contributions from the initial precipitation, x-ray counting, peak deconvolution and calibration uncertainty. Analysis of EPA 1 (Table F-6) indicates the ability of the method to determine the elements Se and Ni with an accuracy of ±10% relative and a precision of 6% relative at a level of 8.7 ppb in a 100 mL sample. Mercury was undetected at 0.4 ppb. The elements Mn and Zn were determined with somewhat reduced precision and accuracy at the levels considered (<10 ppb). The elements Cu and Zn suffered from variable blanks as discussed earlier yielding precision in the region of 15-20% and showing a positive bias at the level of analysis (~10 ppb). The determination of Fe suffered somewhat similar blank problems at the 19 ppb level giving rise to a reduced precision (9% relative) and a positive bias. The data for Pb showed similar behavior to Fe but at a Pb concentration of 35 ppb. The remaining two elements in EPA 1 (Co and V) showed an accuracy better than ±3% and precision in the region of 6% relative. The analysis of 4 ppb Hg in TM 10 serves to indicate the possibilities of the technique for such low concentrations (±20% accuracy with a precision of 20% relative). Thus, at low ppb concentrations, the technique is well-suited to the simultaneous determination of many elements and through the use of solution volumes greater than those used here (100 mL) then the accuracy and precision could be improved upon even further. Accuracy and precision have been similarly assessed but at somewhat higher concentrations (Table F-7).

Thus, the elements Fe, Ni, Zn, Co, and V have been determined at trace levels (20-500 ppb) with an accuracy and precision better than 6% relative. The determination of Cu is similarly precise, but careful blank control is required in order to yield unbiased results. The elements Se and Pb are determined with an accuracy around 10% relative and precision around 7% whereas Hg may be accurately determined (7% relative) but with a much reduced precision (37% relative) at an analyte concentration of 4.4 ppb.

Thus, DBDTC precipitation in conjunction with EDXRF spectrometry is capable of the accurate and precise multielement determination of most of the EPA Priority Pollutant elements at low ppb concentrations in synthetic water samples. The utility of such a method is, however, dependent upon its performance in real water samples.

Analysis of Water Samples

A series of water samples (Appendix A) collected in Colorado comprising two public potable waters (TW1, TW2), nine river or creek samples from many varied locations and three high altitude lake waters (CL, EL, and LE) was analyzed using both DBDTC precipitation/EDXRF and atomic absorption spectrometry. Only Mn, Fe, Ni, Cu, and Zn were determined and the results from this study are shown in Appendix G. In general, close agreement is seen between the results from both methods. This is particularly the case for Mn where the agreement is good over a very wide range of analyte concentrations (2 ppb - 2.5 ppm). Similar agreement is seen in the case of Fe, but the levels do not extend over quite the range seen for Mn. In the case of Ni and Cu, the agreement between methods is excellent despite the fact that the analyte levels are approaching the lower limits of detection for both methods. In most cases, the ability of the two methods to detect elements is very similar. The use of a large volume of sample in the DBDTC/EDXRF method would, of course, enable the LLD to be reduced were that to be necessary. The determination of Zn shows somewhat poorer agreement between the two methods. The determination of trace levels of Zn in complex natural waters using graphite furnace AAS is frequently fraught with difficulty and this is again evident here. Thus, many of the results compare well, but Zn values for some of the creek samples (SP 1, CC 2, and BC) containing large amounts of a concomitant cation e.g., Mn, and/or elevated anion (particularly Cl^-) concentrations show large intermethod disparity. With the knowledge of some of the concomitants in these particular samples from predominantly mining areas, the graphite furnace AAS method is expected to suffer from severe interference particularly for Zn determinations. Thus, the DBDTC/EDXRF method, whose interferences have been found to be very limited and correctable, yields much more reliable data for the complex samples analyzed here. In addition to the ability of the latter method to produce reliable data for trace element concentrations in natural waters it is a truly multielement analytical technique. This latter advantage is of particular benefit in terms of time and simplicity when comparing existing methods of analysis, e.g., AAS.

The overall analytical performance of two precipitation methods (APDC and DBDTC) in conjunction with energy dispersive x-ray fluorescence (EDXRF) spectrometry has been compared. On the basis of that comparison the use of

sodium dibenzyldithiocarbamate precipitation for the preconcentration of trace elements for determination using EDXRF spectrometry is recommended. Such a method is capable of accuracy and precision better than 5% relative when used as a simultaneous multielement technique in the analyte range 10-1000 ppb for the elements Se, Cu, Ni, Fe, Co, Zn, Mn, Hg, Pb, and Tl. In addition to these elements, As and Cr are similarly determinable but only when in the +3 and +6 oxidation states, respectively. The method as described requires only 100 mL of sample to yield the performance cited and 30 min per sample for all the elements is the maximum time required. As more samples are processed, the average analysis time may be markedly decreased making the technique even more attractive for the analysis of all the EPA Priority Pollutant elements in natural waters except Be. The "rugged" nature of the precipitation method along with the automated multielement capability offered by EDXRF spectrometry makes this combination a valuable analytical tool.

APPLICATION TO CHEMICAL SPECIATION

During the response, interference, and evaluation studies, it became evident that the proposed precipitation EDXRF spectrometric method is also capable of yielding speciation information. It is evident from our work and from that of others (7,34) that Cr in the +3 oxidation state is not recovered by dithiocarbamate precipitation. However, we have observed that Cr in the +6 oxidation state is recovered quantitatively using either sodium dibenzyldithiocarbamate (DBDTC) or the ammonium salt of ammonium pyrrolidinedithiocarbamate (APDC), though the latter exhibits reduced and frequently variable recovery. This observation does, of course, make possible the determination of the speciation of Cr in its two naturally occurring oxidation states. This ability to determine Cr(VI) in the presence of Cr(III) and other elements is of particular advantage in the light of the suspected carcinogenicity of Cr(VI) in waters. In addition to the oxidation state speciation of Cr, the presence of other elements capable of existing in mixed oxidation states, such as As and Se, is to be expected in natural waters. We have determined that some of these other elements may also be speciated by oxidation state through the use of selective precipitation and EDXRF spectrometry.

Chromium

The two naturally occurring oxidation states of Cr are +3 and +6. The latter, Cr(VI), is suspected to be carcinogenic and therefore its determination in public potable water supplies is of utmost importance. At least three methods (ICP/AES, AAS, and ASV) exist for the determination of elemental Cr, but these methods give no direct measure of the "state" of that element in the sample. The use of oxidation state-selective preconcentration followed by XRF spectrometry, however, is capable of yielding this information. Thus, it is our experience and that of others (7,34) also, that Cr(III) is not recovered when using dithiocarbamate precipitation. In particular, we refer here to the use of sodium dibenzyldithiocarbamate (DBDTC). However, DBDTC does recover Cr in the +6 oxidation state (heretofore unpublished) yielding a calibration (Table 3) for Cr determinations by

TABLE 3. CALIBRATION DATA FOR THE DETERMINATION OF Cr(VI) USING DITHIOCARBAMATE PRECIPITATION AND EDXRF SPECTROMETRY

	DBDTC	APDC
Calibration slope (cps/μg)	3.1	0.8
Intercept (μg · Cr)	-0.02	+0.1
Correlation coefficient	0.998	0.9821

EDXRF. The use of APDC in conjunction with EDXRF also yields a Cr calibration but recovery is much reduced and is prone to be erratic as reflected in the lower correlation coefficient. We have, therefore, concentrated our efforts upon the use of DBDTC for the recovery of Cr(VI).

Our data suggest that the DBDTC precipitation is entirely specific for Cr(VI) in the presence of Cr(III) enabling separation of these two species. Data are presented in Table H-1 (Appendix H) for the determination of various elements in Certified Reference Materials (CRM), which are prepared using either Cr(III) or mixed Cr(III)/Cr(VI) solutions. The first four CRM solutions (TM 1, TM 10, ERA 1916 and EPA 3) contain mixtures of Cr(III) and Cr(VI). The quoted data, therefore, are for the Cr(VI) content of the samples. It is obvious from these data that future metal standard reference solutions must be produced with better control if meaningful oxidation state data are to be generated from their analysis. Determination of Cr in the remaining five solutions indicates the high specificity of the DBDTC/EDXRF method for Cr(VI). Even when the Cr content is >200 ppb Cr is not detectable providing that the Cr is in the +3 oxidation state. Thus, the DBDTC method yields the true Cr(VI) content in the presence of large excesses of Cr(III). This is further demonstrated by the fact that if CRM sample ERA 1916 is reduced using KI/Ascorbic acid treatment then the Cr is reduced to Cr(III) and Cr is not detectable using DBDTC precipitation EDXRF (Certified Cr value = 315 ppb).

The high specificity of the DBDTC precipitation method for recovery of Cr(VI) enables the collection of the latter with any other elements which are present and are similarly precipitated. After collection of the DBDTC precipitate, any Cr(III) from the original sample solution will remain in the filtrate liquor and will, therefore, be separated from Cr(VI). If this Cr(III) is subsequently collected by some method it may be determined by XRF spectrometry. Alternatively, the filtrate may be analyzed by some other techniques such as AAS. Previous studies (Sec 5, Response Characteristics and Table C-1) have shown that Cr(III) is recovered by methods using an ion-exchange resin-impregnated filter paper (SA-2), oxinate collection or activated carbon (AC) or dithiocarbamate immobilized on controlled pore glass (CPG). The simplest of these methods was the ion-exchange resin-impregnated filter paper procedure (SA-2). The major disadvantage of this

method had been determined and was the influence of interferents upon element recovery. The pre-precipitation of many concomitant ions by DBDTC successfully removes many interferences and renders the SA-2 method applicable in cases where the alkali and alkaline earth elements are not present in high concentrations. In addition to the SA-2 method, the use of simple hydroxide precipitation or feric hydroxide co-precipitation has also be considered for the recovery of Cr(III).

Simple hydroxide precipitation of the Cr(III) was accomplished by adjustment of the pH of the filtrate liquor to 8.0 ± 0.1 with either sodium or ammonium hydroxide. Although a Chromium (III) hydroxide precipitate formed under these conditions and could be collected on a membrane filter the reproducibility of this method was found to be poor. In particular, the recovery of less than 20 μg Cr(III) was erratic. Coprecipitation of Cr(III) with Fe(III) hydroxide was achieved in the following manner. One hundred micrograms Fe(III) was added to the filtrate from the DBDTC precipitation. The pH of this solution was adjusted to 8.00 ± 0.03 with 50% v/v ammonium hydroxide solution and the solution was immediately filtered through a 0.45 μm membrane filter. The method using SA-2 paper was simple and involved passing the filtrate from the DBDTC precipitation seven times through the same 25-mm-diameter ion-exchange resin-impregnated filter paper. All resulting filters were mounted between ¼-mil Mylar films before SRF spectrometry. Energy dispersive XRF spectra were collected over the range 4-14 keV using a silver anode x-ray tube operated in a pulsed mode at 30 kV and 0.30 mA in conjunction with a 0.025 mm Ag foil filter. Calibration data for Cr(VI) by DBDTC and for Cr(III) by the $Fe(OH)_3$ and SA-2 methods are shown in Table 4.

Sensitivity was highest for the DBDTC method, the other two methods showing decreased sensitivity due to either increased matrix absorption ($Fe(OH)_3$, SA-2) or dispersion of the analyte through the thickness of the substrate (SA-2). Despite the lower sensitivity for Cr by the SA-2 method, the simplicity and low blank made this method the one of choice. The large number of variables influencing coprecipitation efficiency in the $Fe(OH)_3$ method meant that the SA-2 method was more easily optimized. Additionally, we have previously studied the SA-2 method and knew its drawbacks. On the basis of the above calibrations for SA-2 and DBDTC, Cr was determined in a series of four Certified Reference Materials. The DBDTC precipitation yielded the Cr(VI) content and the Cr(III) content was determined after repeatedly passing the filtrate through a SA-2 paper. This approach yielded the results shown in Table H-2. From that table it is evident that only one CRM (EPA 3) contains Cr(III) alone. Two other CRM samples (EPA 2 and 10) contain predominantly Cr(III) whereas ERA 1512 contains almost one-third Cr(VI). In general, the total Cr values are less than the certified concentrations. This suggests incomplete collection of either or both Cr species. One possibility is that Cr(III) recovery may be decreased if an exchangeable concomitant is not precipitated by DBDTC. Such an influence might be equated from Al^{3+} or Ca^{2+} ions. The results for Cr in EPA 2 and ERA 1512 show better accuracy, suggesting that the method had potential for the speciation of Cr in natural waters. The simplicity of this overall approach makes the DBDTC/SA-2 method particularly attractive and the possibility for automation of such a system may be of advantage.

TABLE 4. EDXRF CALIBRATION DATA FOR THREE METHODS OF PRECONCENTRATION OF Cr

	DBDTC	$Fe(OH)_3$	SA-2
Species recovered	Cr(VI)	Cr(III)	Cr(III)
Sensitivity (cps/μg Cr)	3.1	2.1	1.3
Intercept (μg Cr)	-0.02	3.2	0.2

Arsenic

Similar to the case for Cr, As has two naturally occurring oxidation states in water systems, As(III) and As(V), i.e., arsenite and arsenate. It is, as in the case of Cr, our experience and that of others (7, 34) that only one of these species is precipitated by DBDTC. In this case As(III) is recovered in the presence of As(V) with a high degree of selectivity and perhaps total specificity. Data from the recovery of As from several Certified Reference Materials (CRM) are summarized in Table H-3 indicating that, as for Cr, some of the CRM solutions (EPA 1916, EPA 3, and CSL 2291) contained As in mixed oxidation states. The remaining solutions all contained As in the +5 oxidation state and, therefore, showed no detectable As signal after preconcentration by DBDTC. The high selectivity for As(III) is notable in EPA 2 which contains no detectable As despite an As(V) content of 182 ppb.

Having shown the selectivity of the method for As(III) it is necessary to demonstrate the ability of the method to yield full As speciation data through the determination of As(V) also. This may be accomplished through the reduction of As(V) to As(III) and subsequent determination of As(III) using dithiocarbamate precipitation. The reduction conditions must be sufficiently selective to enable conversion of As(V) to As(III) without the possibility of the reaction continuing through to the zerovalent or, worse still, the -3 oxidation state. In the latter case the loss of As as the volatile hydride (arsine) would be a distinct possibility. The reported use of KI/Ascorbic acid (34) seems to offer the required selectivity but has the disadvantage of being rather slow. Despite this latter reservation, we have used these conditions with some success as shown by the data in Table H-4 where the results from the analysis of several CRM solutions both before and after reduction are presented. The data show approximately 90% recovery of As in all cases except for EPA 2 where 82 ppb As were found compared to the expected concentration of 182 ppb As. The possibility of much poorer recovery in this particular sample does, of course, exist but the presence of a simple typographical error upon the certificate cannot be ruled out. Thus, the use of selective precipitation followed by this particular reduction step with subsequent precipitation by DBDTC is capable of providing the As(III) and As(V) content of synthetic water samples.

Modified As(V) reduction conditions in which the reductant concentrations were increased and the boiling time lengthener were also investigated (Section 4, Reduction Conditions). Duplicate determinations of As(III) and As(V) were carried out for CRM samples EPA 10, EPA 1, EPA 1512, and CSL 2291 using the modified reduction step and DBDTC precipitation. In addition, As(III) and (V) in CRM samples EPA 2 and 3 were determined in quadruplicate (Table H-5). Using the modified reduction conditions the accuracy of the method is good. In the cases of EPA 2, 3, and 10 CRM solutions only As(V) is present whereas both As(III) and As(V) are present in the remaining solutions. Solutions EPA 1 and 2 and ERA 1512 gave high accuracy (better than 5%) and precision around 5% relative for EPA 2. In general, the recovery of As(V) using the modified conditions is improved when compared with the original conditions. The method is demonstrated to yield adequate data for the speciation of As on aqueous solutions at the levels considered.

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APPENDIX A

SAMPLE LOCATION

SP 1	South Platte upstream Denver (May*)
SP 2	South Platte downstream Denver
SP 3	South Platte upstream Denver
CC 1	Clear Creek above North Fork confluence
CC 2	North Fork Clear Creek above confluence
CC 3	Clear Creek upstream Golden
TW 1	Tap water, Nederland
TW 2	Tap Water, Denver University
SSV	South St. Vrain at Lyons (May)
BC	Bear Creek upstream Morrison
BDC	Boulder Creek upstream Boulder
CL	Carter Lake, Longmont (May)
EL	Evergreen Lake, Evergreen
LE	Lake Eldora, Nederland

* All in July except where shown (May).

APPENDIX B

CERTIFIED REFERENCE MATERIALS

CRM Code	Source	Description
CSL 2291	Chemical Services Laboratory P.O. Box 281 Largo, FL 33540	Heavy Metals Standard
ERA 1615, 1512	Environmental Resource Assoc. 120 East Sauk Trail Chicago Heights, IL 60411	Potable Water
ERA 1916	Environmental Resource Associates	Waste Water/Trace Metals
TM 1, TM 10 Ref # WS378	U.S. EPA Environmental Monitoring & Support Laboratory Cincinnati, OH 45268	Concentrates 1 & 10 Trace Metal
EPA 1, 2, & 3 Ref WP476E	EPA Environmental Monitoring & Support Laboratory	QC Check Samples

Each solution was prepared according to the suppliers' instructions.

APPENDIX C

TABLE C-1. FIGURE OF MERIT DATA FOR PRECONCENTRATION METHODS

Method	Spectrometer		Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
AC	EDS	Sens.*	0.4	0.6	0.9	0.9	2.3	1.6	3.4	NRζ	NR	**¶	**	0.1	1.2	0.4	1.5
		LLDΨ	1.7	1.4	8.6	0.4	8.1	2.0	3.9	NR	NR	**	**	25.0	1.5	1.8†	0.8
		%RSD§	13.4	10.1	12.4	10.7	6.4	12.0	13.7	NR	NR	**	**	5.9	3.4	20.5	5.5
	WDS	Sens.	35.8	48.4	7.9	5.1	12.0	2.0	3.4	NR	NR	1.9	2.0	1.5	10.0	4.6	11.0
		LLD	1.3	0.3	8.9	0.5	2.3	6.0	4.9	NR	NR	1.8	2.6	6.8	0.6	1.3†	0.7
		%RSD	5.0	2.8	11.7	6.8	7.5	6.6	4.7	NR	NR	2.9	14.8	12.6	9.5	10.7	3.4
APDC	EDS	Sens.	NR	NR	2.9	2.1	4.7	5.6	2.5	9.4	8.2	**	**	0.2	3.8	NR	3.0
		LLD	NR	NR	0.3	0.4	1.7	0.4	0.3	0.3	0.6	**	**	14.0	0.3	NR	0.5
		%RSD	NR	NR	4.8	4.5	5.5	5.5	10.9	6.4	6.8	**	**	27.0	6.1	NR	4.7
	WDS	Sens.	NR	NR	15.8	20.0	19.0	12.0	19.0	15.0	24.0	2.2	2.4	2.2	12.0	NR	14.0
		LLD	NR	NR	0.3	0.3	1.5	0.8	0.3	0.5	2.6	3.9	2.8	3.0	0.3	NR	0.4
		%RSD	NR	NR	3.4	3.4	4.2	6.3	8.0	4.1	7.3	4.5	10.9	6.8	4.1	NR	3.1
CPG	EDS	Sens.	0.3	0.15	0.4	1.1	1.5	0.8	2.1	NR	NR	**	**	1.2	0.5	1.5	0.6
		LLD	1.8	2.7†	4.3	0.8	0.5	1.0	2.1	NR	NR	**	**	2.6†	1.3	2.0	3.3
		%RSD	10.7	12.5	19.7	9.9	8.5	11.5	11.0	NR	NR	**	**	15.0	8.5	8.9	7.0
	WDS	Sens.	2.4	6.2	2.9	5.1	4.3	4.3	4.1	NR	NR	1.3	1.4	1.4	5.7	8.7	4.3
		LLD	1.6	0.5†	2.6	0.3	0.9	1.0	0.9	NR	NR	6.0	4.3	5.0†	0.8	0.7	2.3
		%RSD	11.1	5.9	24.2	4.1	11.6	7.9	10.2	NR	NR	4.3	11.4	7.8	8.7	11.8	8.0
DBDTC	EDS	Sens.	NR	1.3	2.2	2.9	3.3	3.6	3.7	6.2	6.2	**	**	1.0	2.7	0.9	2.3
		LLD	NR	0.4	0.4	0.2	0.4	0.4	0.4	0.2	0.3	**	**	1.0	0.4	1.1	0.6
		%RSD	NR	2.9	3.0	4.0	3.0	2.2	4.6	3.8	4.8	**	**	5.0	4.2	2.3	7.0
	WDS	Sens.	NR	16.0	4.4	8.2	11.1	12.2	24.0	9.1	8.9	4.5	4.0	4.9	2.7	7.4	3.4
		LLD	NR	0.3	3.4	0.3	0.3	0.9	0.4	0.8	0.4	2.0	2.1	0.9	0.6	0.7	0.8
		%RSD	NR	5.7	9.9	6.9	1.6	4.6	5.0	7.6	4.8	8.0	28.9	2.3	4.2	5.2	3.1
NaDDC	EDS	Sens.	NR	NR	2.1	5.7	5.4	7.6	3.8	NR	NR	**	**	1.0	2.6	NR	3.9
		LLD	NR	NR	0.9†	0.4	0.3	0.5	2.2	NR	NR	**	**	20.0	0.4	NR	0.2
		%RSD	NR	NR	4.9	4.5	1.6	9.1	11.9	NR	NR	**	**	7.0	13.0	NR	5.6
	WDS	Sens.	NR	NR	19.3	5.5	5.3	2.6	10.0	NR	NR	2.3	2.5	2.1	7.7	NR	16.0
		LLD	NR	NR	0.9†	0.5	0.3	0.4	1.4	NR	NR	2.3	3.5	4.6	0.7	NR	0.2
		%RSD	NR	NR	5.5	8.8	6.5	4.4	9.7	NR	NR	5.1	10.4	17.4	17.6	NR	5.7

TABLE C-1. Continued.

Method	Spectrometer		Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
PVP-T	EDS	Sens.	NR	NR	NR	NR	NR	1.1	NR	0.3	3.0	**	**	NR	1.2	NR	0.8
		LLD	NR	NR	NR	NR	NR	1.7†	NR	8.3	0.4	**	**	NR	1.6	NR	3.9
		%RSD	NR	NR	NR	NR	NR	8.0	NR	13	3.0	**	**	NR	3.0	NR	22.0
	WDS	Sens.	NR	NR	NR	NR	NR	1.7	NR	0.8	1.4	0.7	NR	NR	1.2	NR	1.3
		LLD	NR	NR	NR	NR	NR	2.5†	NR	13.0	1.5	17.5	NR	NR	1.5	NR	5.3
		%RSD	NR	NR	NR	NR	NR	5.7	NR	18.0	3.1	19.0	NR	NR	6.0	NR	20.2
SA-2	EDS	Sens.	0.6	0.9	1.4	3.5	3.0	4.9	3.3	NR	NR	**	**	NR	0.2	1.6	2.9
		LLD	0.3	0.4	0.1	0.4	0.5	3.0	2.8	NR	NR	**	**	NR	13.0	0.6	0.5
		%RSD	5.8	4.6	12.7	6.0	7.0	13.0	6.0	NR	NR	**	**	NR	21.0	12.0	1..4
	WDS	Sens.	55.9	32.5	14.2	7.0	10.0	12.0	3.0	NR	NR	1.4	2.2	NR	0.7	12.0	14.0
		LLD	0.2	0.5	1.9	0.6	1.2	1.0	9.6	NR	NR	6.0	4.0	NR	4.0	0.6	0.6
		%RSD	6.3	4.3	12.5	4.8	3.2	13.0	4.9	NR	NR	15.0	6.4	NR	14.4	10.2	14.9

* Sensitivity, i.e., the slope (cps·μg^{-1}) of the single element calibration line.

ζ Not recovered.

¶ Not determined due to EDS anode material (Ag).

Ψ Lower limit of detection as defined by Currie (Anal. Chem., 1968, 40, 586).

† Linear ranges extend to 100 μg except for † († = 50 μg).

§ Percent relative standard deviation as determined from 5 replicate samples at 300 μg·L^{-1}.

APPENDIX D

TABLE D-1. EFFECT OF INTERFERENTS ON THE DETERMINATION OF SEVERAL ELEMENTS USING PRECONCENTRATION BY OXINE AND ACTIVATED CARBON

Element Interferent	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
NaCl	0	0	-12	0	0	0	0	*	*	0	13	0	0	4.6	0
Ca	-14	0	-13	0	0	0	0	*	*	0	-9.9	0	0	0	0
Cr	**	-61	0	0	-10	0	5	*	*	0	0	0	0	0	0
Mn	0	**	-11	0	-9.5	0	0	*	*	0	-13	12	0	4.6	0
Fe	40	0	**	0	0	0	0	*	*	0	0	0	0	0	0
Co	0	0	0	**	-33	0	0	*	*	0	-10	-13	0	-4.4	-6.6
Cu	0	0	0	0	9.9	**	-21	*	*	0	0	0	0	0	-7
Zn	0	0	0	0	0	0	**	*	*	0	0	0	0	-7.8	0
Cd	0	0	0	0	0	0	0	*	*	0	**	-34	0	0	0
Pb	0	0	0	0	0	0	0	*	*	0	17	0	0	0	**

* Not recovered.

** Not possible.

TABLE D-2. EFFECT OF INTERFERENTS ON THE DETERMINATION OF SEVERAL ELEMENTS USING AMMONIUM PYRROLIDINEDITHIOCARBAMATE

Element Interferent	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
NaCl	*	*	-7.5	0	0	-2	0	0	-20	0	0	0	0	*	0
Ca	*	*	0	0	0	-3.4	0	0	0	0	-12	0	0	*	0
Cr	**	*	17	0	0	-3.5	0	0	18	2.6	-12	0	0	*	0
Mn	*	**	0	-3	-8.5	0	0	0	0	0	-13	0	0	*	0
Fe	*	*	**	-3.5	0	-4	10	-7	0	-2.4	0	0	0	*	0
Co	*	*	-23	**	-67	-5.5	0	0	0	-3.6	11	0	0	*	0
Cu	*	*	0	0	0	**	-24	-5	-9.2	0	0	0	0	*	0
Zn	*	*	0	0	0	-3.7	**	0	0	0	0	-7.6	-2.8	*	0
Cd	*	*	-14	-3	-8.7	-6.9	0	0	0	0	**	-55	0	*	0
Pb	*	*	0	3.7	0	-1.3	0	106	0	0	0	12	0	*	**

* Not recovered.

** Not possible.

TABLE D-3. EFFECT OF INTERFERENTS ON THE DETERMINATION OF SEVERAL ELEMENTS USING PRECONCENTRATION BY DITHIOCARBAMATE IMMOBILIZED ON CONTROLLED PORE GLASS

Element Interferent	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
NaCl	0	0	-11	34	0	0	0	*	*	0	0	-9.7	0	-9.8	31
Ca	0	0	32	28	9.6	0	0	*	*	0	19	0	0	-8.9	26
Cr	**	35	-13	-29	0	0	0	*	*	0	-13	0	20	0	0
Mn	0	**	-10	0	13	0	-15	*	*	0	0	0	0	0	0
Fe	0	0	**	40	9	0	15	*	*	0	9.5	0	-12	0	0
Co	0	0	-10	**	-31	0	-25	*	*	0	0	-8	0	12	0
Cu	0	-29	7.6	0	-6.9	**	-28	*	*	0	0	0	0	0	0
Zn	0	0	0	0	0	0	**	*	*	0	0	0	0	-10	0
Cd	0	0	0	-16	0	0	0	*	*	0	**	-57	-12	0	0
Pb	0	-31	-7.5	-14	-7.4	0	0	*	*	0	8.7	0	0	-28	**

* Not recovered.

** Not possible.

TABLE D-4. EFFECT OF INTERFERENTS UPON THE DETERMINATION OF SEVERAL ELEMENTS USING SODIUM DIBENZYLDITHIOCARBAMATE

Element / Interferent	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
NaCl	*	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	*	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cr	**	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mn	*	**	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe	*	-32	**	30	0	0	0	0	0	0	0	0	0	0	0
Co	*	-21	-29	**	-49	-39	0	0	0	0	0	0	0	0	0
Cu	*	-33	-14	0	0	**	0	0	0	0	0	0	0	0	0
Zn	*	-17	0	0	0	0	**	0	0	0	0	0	0	0	0
Cd	*	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pb	*	0	0	0	0	0	0	0	0	0	**	0	0	0	0
														164	**

* Not recovered.

** Not possible.

TABLE D-5. EFFECT OF INTERFERENTS ON THE DETERMINATION OF SEVERAL ELEMENTS USING PRECONCENTRATION BY SODIUM DIETHYLDITHIOCARBAMATE

Element Interferent	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
NaCl	*	*	0	0	0	0	18	*	*	0	0	0	0	*	0
Ca	*	*	0	0	0	0	0	*	*	0	0	4.2	0	*	0
Cr	**	*	0	0	-4.8	0	0	*	*	0	0	0	0	*	0
Mn	*	**	0	-3.6	0	0	0	*	*	0	0	0	0	*	0
Fe	*	*	**	0	-4.8	0	0	*	*	0	-18	0	-8	*	0
Co	*	*	-12	**	-104	0	0	*	*	0	0	10	0	*	0
Cu	*	*	0	0	0	**	0	*	*	0	16	0	0	*	-9
Zn	*	*	0	3.5	12	0	**	*	*	0	0	0	0	*	0
Cd	*	*	0	0	0	-5	0	*	*	0	**	-40	0	*	0
Pb	*	*	0	0	0	0	-22	*	*	0	0	0	0	*	**

* Not recovered.

** Not possible.

TABLE D-6. EFFECT OF INTERFERENTS ON THE DETERMINATION OF SEVERAL ELEMENTS USING POLY(VINYLPYRROLIDONE)-THIONALIDE

Element Interferent	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
NaCl	*	*	*	*	*	0	*	0	0	0	*	*	0	*	84
Ca	*	*	*	*	*	0	*	0	0	0	*	*	0	*	0
Cr	**	*	*	*	*	0	*	0	0	0	*	*	0	*	0
Mn	*	**	*	*	*	0	*	0	0	0	*	*	0	*	0
Fe	*	*	**	*	*	0	*	0	0	0	*	*	0	*	0
Co	*	*	*	**	*	0	*	0	18	0	*	*	0	*	0
Cu	*	*	*	*	*	**	*	0	0	0	*	*	0	*	117
Zn	*	*	*	*	*	-18	**	0	-15	0	*	*	0	*	0
Cd	*	*	*	*	*	0	*	0	0	0	**	*	0	*	0
Pb	*	*	*	*	*	0	*	100	0	0	*	*	0	*	**

* Not recovered.

** Not possible.

TABLE D-7. EFFECT OF INTERFERENTS ON THE DETERMINATION OF SEVERAL ELEMENTS USING PRECONCENTRATION BY RESIN-IMPREGNATED FILTER PAPERS

Element Interferent	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sb	Hg	Tl	Pb
NaCl	0	0	0	2	0	-8	0	*	*	0	-3.7	*	98	-2.7	-40
Ca	-27	-62	-65	-30	-7.8	-70	-24	*	*	-9	-169	*	0	9.3	-64
Cr	**	5	0	-2	0	0	0	*	*	0	-8.7	*	0	-3.8	0
Mn	0	**	0	0	0	0	0	*	*	0	0	*	0	0	0
Fe	0	0	**	0	0	0	0	*	*	-14	0	*	0	-2.6	-12
Co	0	0	0	**	-18	0	0	*	*	0	0	*	0	-2.9	0
Cu	0	0	-6.1	0	0	**	-33	*	*	0	0	*	0	2.9	0
Zn	0	3	8.5	3	0	0	**	*	*	-12	0	*	52	0	-12
Cd	0	0	0	0	4.2	0	0	*	*	0	**	*	50	-24	0
Pb	0	-4	-9.6	0	0	0	0	*	*	0	0	*	0	-92	**

* Not recovered.

** Not possible.

APPENDIX E

TABLE E-1. THE RATING OF PRECONCENTRATION METHODS FOR XRF SPECTROMETRY ON THE BASIS OF RESPONSE CHARACTERISTICS

Method	R_{EDXRF}	R_{WDXRF}	R_{TOT}	Rank
AC	23	33	56	3
APDC	25	33	58	2
CPG	21	27	48	5
DBDTC	40	38	78	1
NaDDC	20	22	42	6
PVP-T	11	12	23	7
SA-2	22	28	50	4

$$R_{EDXRF,\ RWDXRF} = \sum_{i=1}^{n} \ln \frac{\text{(linear range)}}{\sqrt{2\pi e} \times s}$$

where

n = number of elements recovered
linear range = 100 or 50 μg minus LLD
Standard deviation (s) was determined at 300 ppb

TABLE E-2. RATING AND RANKING OF THE METHODS ON THE BASIS OF TOTAL INTERFERENCE EFFECTS

Method	R_{IA}	$Rank_A$
AC	31	2
APDC	44	4
CPG	62	6
DBDTC	39	3
NaDDC	30	1
PVP-T	50	5
SA-2	90	7

TABLE E-3. RATING AND RANKING OF THE METHODS ON THE BASIS OF CHEMICAL INTERFERENCE EFFECTS

Method	R_{IB}	$Rank_B$
AC	18	3
APDC	20	4
CPG	43	6
DBDTC	11	1
NaDDC	13	2
PVP-T	30	5
SA-2	77	7

TABLE E-4. THE CONTRIBUTION OF CHEMICAL INTERFERENCE TO SEVERAL PRECONCENTRATION METHODS

Method	Percent chemical interference
AC	58
APDC	46
CPG	69
DBDTC	28
NaDDC	43
PVP-T	60
SA-2	86

APPENDIX F

TABLE F-1. DBDTC CALIBRATION PARAMETERS

Element	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Hg	Tl	Pb
Slope*	3.1	3.6	5.6	6.7	8.2	9.8	11.4	15.8	14.4	9.3	9.1	10.5
Intercept†	-0.02	0	+1.5	+0.07	-0.03	+0.4	+0.49	-0.27	-0.13	-0.16	+0.11	+0.4
Correlation coefficient	0.998	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999

* cps/μg.

† μg.

TABLE F-2. APDC CALIBRATION PARAMETERS

Element	Cr	Fe	Co	Ni	Cu	Zn	As	Se	Hg	Pb
Slope*	0.8	5.8	6.9	8.6	10.8	11.1	13.7	15.2	9.2	9.3
Intercept†	+0.1	+1.06	+0.03	-0.12	+0.24	+0.23	-0.32	-0.25	-0.17	+0.99
Correlation coefficient	0.982	0.999	0.999	0.999	0.999	0.998	0.999	0.997	0.999	0.997

* cps/μg.

† μg.

TABLE F-3. ANALYSIS OF CERTIFIED REFERENCE MATERIALS USING APDC PRECIPITATION [All values are ppb ($\mu g\ L^{-1}$)]

Element	ERA 1916*		ERA 1512*		EPA 2*		EPA 3*	
	Exptl.†	Cert.¶	Exptl.	Cert.	Exptl.	Cert.	Exptl.	Cert.
Se	28,28	25	26,24	25	50,55	48	17,16	16
Cu	381,404	430	-	-	364,402	374	42,39	37
Fe	179,190	200	534,472	500	746,820	796	79,81	78
Ni	167,179	165	-	-	170,182	165	89,90	96
Zn	243,250	335	-	-	294,320	478	<5	26
Cr	778,803	315	n.d.§	190	n.d.	304	n.d.	65
Co	230,247	235	-	-	330,357	348	99,95	96
As	20,16	84	n.d.	19	n.d.	182	n.d.	61
Hg	15,14	1.7Ψ	4.6,3.4	2.5	9.7,10.5	7.6	5.7,5.9	4.4
Pb	118,132	135	40,41	38	338,372	383	96,101	113

* CRM designation (see Appendix B).

† Duplicate experimental values (ppb).

¶ Certified value (ppb).

§ Not detected.

Ψ Cold vapor AA value - 13 ± 3 ppb (independent analysis).

TABLE F-4. ANALYSIS OF CERTIFIED REFERENCE MATERIAL ERA 1916 USING DBDTC/EDXRF

Element	Found (ppb)		Percent of certificate
Co	233	237	100
Cu	426	450	102
Fe	187	199	97
Pb	122	136	96
Mn	234	220	72
Hg	21	17	112
Ni	174	183	108
Se	26	26	104
Tl	70	70	108
Zn	328	341	100
V	55		92
Ti	170		103
Cr/As	mixed oxidation states		

TABLE F-5. ANALYSIS OF CERTIFIED REFERENCE MATERIALS USING DBDTC/EDXRF
[all figures are $\mu g\ L^{-1}$ (ppb)]

Element	CSL 2291*		EPA TM 1		EPA TM 10		ERA 1512		ERA 1615	
	Exptl.†	Cert.¶	Exptl.	Cert.	Exptl.	Cert.	Exptl.	Cert.	Exptl.	Cert.
Se	4.8,5.3	5	5,5.8	6	5.6,6.7	7.3	21,26	25	28,28	31
Hg	n.d.§	0.5	n.d.	1.4	2.9,3.1	4	2Ψ,2Ψ	2.5	4.3,4.0	3.7
Pb	54,52	50	23,23	22	44,37	38	36,42	38	42,41	25
As	38,37	50	n.d.	22	n.d.	40	n.d.	19	n.d.	25
Fe	--		--		--		478,530	500	447,451	450
Mn	--		--		--		243,276	250	280,272	260

* CRM designation (see Appendix B).

† Duplicate experimental values (ppb).

¶ Certificate values (ppb).

§ Not detected.

Ψ Detected but not quantified.

TABLE F-6. ACCURACY AND PRECISION OF DBDTC/EDXRF AT LOW ppb LEVELS

Element	Mean* (ppb)	% RSD†	Certificate value (ppb)	% Certificate¶
EPA 1				
Se	7.8	6.1	8.7	90
Cu	12.3	17	8.7	141
Fe	19	8.9	16	119
Ni	9.5	6.4	8.7	109
Zn	8.6	18	6.1	141
Mn	6.7	6.1	7.9	85
Co	30.8	6.6	30	103
Hg	n.d.	-	0.4	-
Pb	34.6	13.4	30	115
V	77	6.2	78	99
TM 10				
Se	7.0	9.6	7.3	96
Hg	4.8	22	4	120
Pb	41	10.5	38	108

* Mean of 8 duplicate determinations.

† Computed from sample standard deviation.

¶ (Mean/certificate) × 100.

TABLE F-7. ACCURACY AND PRECISION OF DBDTC/EDXRF METHOD AT TRACE LEVELS

Element	Mean* (ppb)	% RSD†	Certificate value (ppb)	% Certificate¶
EPA 3				
Se	14.1	7.5	16	88
Cu	43	5.7	37	116
Fe	78.8	4.7	78	101
Ni	101	4.6	96	105
Zn	26.2	5.8	26	100
Mn	41	6.6	47	87
Co	92	4.4	96	96
Hg	4.7	37	4.4	107
Pb	123	6.6	113	109
V	442	2.3	470	94

* Mean of 8 duplicate determinations.

† Computed from sample standard deviation.

¶ (Mean/certificate) × 100.

APPENDIX G

TABLE G-1. THE ANALYSIS OF NATURAL WATERS BY DBDTC PRECIPITATION/EDXRF AND ELECTROTHERMAL ATOMIZATION/AAS ($\mu g\ L^{-1}$)

Sample	Mn		Fe		Ni		Cu		Zn	
	XRF*	AA†	XRF	AA	XRF	AA	XRF	AA	XRF	AA
SP 1	96	104	22	22	4	3.7	10	4	76	17
SP 2	195	158	75	38	18	23	5	6	44	30
SP 3	114	182	59	56	0.9	2.3	n.d.¶	n.d.	7	n.d.
CC 1	450	450	46	42	0.9	2.2	1.8	5	61	51
CC 2	2400	2700	15	22	20	25	5	14	1059	342
CC 3	360	338	76	62	1.2	2.4	6	6	104	92
TW 1	1.4	n.d.	53	48	n.d.	0.5	15	17	21	15
TW 2	39	37	82	82	0.8	2.9	30	46	59	19
SSV	3	5	25	52	0.7	0.5	n.d.	n.d.	7.5	1
BC	7	5	75	96	2	3	1.5	4	190	74
BDC	2	2	59	50	0.4	0.5	n.d.	n.d.	12	2
CL	0.6	n.d.	21	22	2	5	9	3	48	2
EL	11	12	81	132	0.3	1.2	n.d.	n.d.	55	47
LE	3.4	1	119	122	n.d.	0.6	n.d.	n.d.	4	n.d.

* DBDTC/EDXRF.

† Carbon furnace ETA/AA.

¶ Not detected.

APPENDIX H

TABLE H-1. RECOVERY OF Cr FROM CERTIFIED REFERENCE MATERIALS SOLUTIONS USING DBDTC/EDXRF

Chromium	TM 1	TM 10	ERA 1916	EPA 3	ERA 1512	ERA 1615	EPA 1	EPA 2	CSL 2291
Found	2, 3	18, 15	232, 228	26, 18	1, 2	nd*, 1.3	nd, nd	nd, nd	nd, 1.2
Certified value†	11	42	315	65	190	260	4.4	304	50

* Not detected.

† Values are for duplicate determinations expressed in ppb ($\mu g\ L^{-1}$).

TABLE H-2. DETERMINATION OF Cr(III) AND Cr(VI) IN CERTIFIED REFERENCE MATERIALS [all values are ppb ($\mu g \cdot L^{-1}$)]

	Sample			
	EPA 2	EPA 3	EPA 10	EPA 1512
DBDTC Cr(VI)	8	0	3	31
SA-2 Cr(III)	130	42	30	74
Total Cr Found	138	42	33	105
Certified Cr (Total)	152	65	42	95

TABLE H-3. RECOVERY OF ARSENIC FROM CERTIFIED REFERENCE MATERIALS SOLUTIONS USING DBDTC/EDXRF

Arsenic	ERA 1916	EPA 3	CSL 2291	TM 1	TM 10	ERA 1512	ERA 1615	EPA 1	EPA 2
Found	21, 23	47, 49	38, 37	3, 4	nd*, <2	<2, <2	nd, nd	nd, nd	nd, nd
Certified value†	84	61	50	22	40	19	25	24	182

* Not detected.

† Values are for duplicate determinations expressed in ppb (μg L^{-1}).

TABLE H-4. THE RECOVERY OF As FROM MIXED As(V)/As(III) SOLUTION

	CRM			
Arsenic	ERA 1916	EPA 2	ERA 1615	CSL 2291
Found	21, 23	nd*, nd	nd, nd	38, 37
Found after reduction	70, 75	82, 82	20, 23	50, 43
Certified value†	84	183	24	50

* Not detected.

† All values are for duplicate determinations expressed in ppb.

TABLE H-5. THE DETERMINATION OF As(III) AND As(V) USING DBDTC/EDXRF

	As III	As V	Total As	Certified As value (total)
EPA 1*	3, 3	18, 20	21, 23	22
EPA 10	0, 0	26, 36	26, 36	40
EPA 1512	5, 6	11, 14	16, 20	19
CSL 2291	36, 38	6, 6	42, 44	50
EPA 2	nd†	100, 93, 88, 96	94 ± 5¶	91
EPA 3	nd	54, 58, 48, 53	53 ± 4	61

* CRM designation (Appendix B). All figures are ppb ($\mu g\ L^{-1}$).

† Not detected.

¶ Mean ± are standard deviation for four replicates.